

THE CHEMISTRY OF DRYING OILS

OIL & COLOUR CHEMISTRY MONOGRAPHS

Edited by R. S. Morrell, M.A., Ph.D., F.I.C.

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BY

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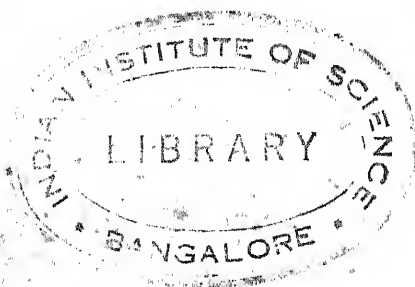
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EDITOR'S NOTE

RECENT criticism of the literature of Chemical Technology will make authors reflect as to whether they are offering to their readers up-to-date information which is of real value. The writers of this series have had primarily in their minds the presentation of published information on properties or processes. The facts have been selected from scientific and technological literature, and what is improbable or misleading has been rejected. Criticism of literature on such lines by those who are familiar with the subject must be of real value. It is only in this way that a chemico-technological writer can offer to his readers descriptions of processes and of plant. In the series of nine monographs the authors have special and direct knowledge of their subjects, and they are either manufacturers or employees of manufacturers. The chemist and the craftsman have often to deal with problems which are at present not appreciated or understood the one by the other. The problems which face the craftsman are often too complex to be solved by the chemist, however well informed he may be. At the same time, the reader with craftsman's experience will admit the importance of the presentation of the most recent published scientific literature, especially if such has been selected by those acquainted with technological requirements. The craftsman's method of trial and error is an exhausting mode of investigation. He wants to produce an effect which can be obtained under a wide margin of varying conditions. Often he has only his own experience to guide him. It is then that a knowledge of chemical and physical properties of the ingredients or the behaviour of admixtures is of great value. Each works chemist will be able to select from a summary of published literature what will suit his own factory requirements. It is recognised that factory conditions vary greatly, and it may occur that a detailed description of a plant in use in one factory may be quite unsuitable for another factory.

It may seem out of date to refer to the old belief in the special value of the craftsman's skill, but it must be admitted that it is a skill which cannot be stated in words. Even in the laboratory no printed directions, however carefully compiled, can be considered to replace the personal directions of the teacher.

Perhaps the most serious defect in chemico-technological literature is due to authors endeavouring to write on subjects on which they have partial practical and scientific knowledge. It is rare to find an author who can present the progress of any large industry with conviction drawn from first-hand knowledge. The Paint and Varnish Industry is now so specialised that the subject requires

treatment by a large number of experts. If superficial treatment were frequent in published chemico-technological literature it would do great harm to the scientist and would tend to retard the association of science and industry which ought to be encouraged so much in this country. With proper appreciation of the standpoint for the technological writer the criticisms of an expert are of value.

Under these conditions it is to be hoped that the series will succeed in giving valuable information and instruction to chemists and works managers in the branches of the industry in which they are engaged.

R. S. M.

AUTHORS' PREFACE

THE explanation of the drying of linseed oil has not yet been satisfactorily given. In spite of the comparative antiquity of the use of linseed oil in Europe as a paint medium, the changes which occur during the drying process have only recently been made the subject of careful investigation. The fact that oxidation with simultaneous or subsequent coagulation takes place will indicate some of the difficulties of arriving at an adequate conclusion; even a satisfactory explanation of the setting of gelatin is not yet forthcoming. An attempt has been made to collect information on the chemical composition of the commoner drying oils and to trace the connection between the composition and properties, especially with reference to the oxygen absorption and the behaviour of the products of oxidation. The problems of the setting of oil films and the behaviour of linoxyn are discussed, and comparison has been made with colloid jellies, of which gelatin is typical. From the mass of detail presented it is evident that much has yet to be considered before a satisfactory explanation of the phenomenon of drying can be presented. The durability of the oxidation products with their valuable protective powers has to be assured, and in this respect many drying oils show weakness, in spite of careful attention paid to the selection of proper materials and to the control of the process of setting.

A number of industries besides paint and varnish make use of drying oils. The linoleum industry, the electrical engineering industry and the leather trades are the most important examples.

The extraction of drying oils from their seeds is associated with the production of cattle feed cake. It is a valuable characteristic of "Linum" that all parts of the plant fibre and seed are of industrial importance; the treatment of the fibre is the basis of the linen industry. The supply of oil seeds is annual from almost all the continents of the globe.

In spite of their admitted defects, drying oils, and especially linseed oil, will yet for a long time retain their popularity as cheap protecting media, easy of application, conferring gloss and being essential for most decorative schemes. The claims of the forms of soluble cotton esters to displace linseed oil are becoming more persistent. The asserted superiority of durability, with economy of time of application, has to be balanced in some cases against the difficulties of preparation of suitable ground coats and the maintenance of elasticity and adherence of the films. The employment of new and blended solvents, many of them highly volatile, creates a prejudice against their use in ordinary decorative schemes, where

slowness of setting and freedom under the brush are essential. It is possible that in time a satisfactory blending of solvents may be attained so that the present mode of spraying may be replaced by the ordinary brush application. Nevertheless the difficulties of application of superimposed coats are admittedly great. In Mr. Sproxtton's "Cellulose Varnishes" the claims of cotton films are excellently stated and the readers of this volume will have an opportunity of contrasting the two media and forming their own opinions. The principles put forward by Mr. Tudor Hart (Society of Mural Decorators and Painters in Tempera, 1922) for applying media for tempering artists' pigments should not be overlooked. "Any medium which fails to allow of exactness and subtlety of blending, permanence of tone and colour and delicacy of form must be rejected; moreover, any medium, the binding quality of which is only temporary or subject to alteration, is unsuitable for artists' use. Experience has shown that drying oils do not satisfy completely these requirements, but they go far, especially when blended with other media, to produce in the hands of the artist an expression of beauty present in his imagination." To the artist permanence of the effect is often subsidiary, but to the craftsman it is of the highest importance. Beauty and efficiency ought to occur together and are the ideal outcome of effort as portraying strength.

In the arrangement of the material in this volume the authors have laid special stress on the importance of the chemical and physical properties in relation to chemical composition; therefore the composition of the drying oils and their component acids has been dealt with very fully, before discussing the common properties which are manifested in the industries in which drying oils are employed. Emphasis must be laid on the descriptions of typical published processes. A works chemist, who recognises the special peculiarities of his own works conditions, will be able to obtain information which he can easily adapt. The student will gain an insight into the present position of the drying oil industry, and in some cases can take advantage of details provided which will enable him to produce materials under works conditions.

The section on the Linoleum industry has been revised by an expert (Mr. S. Stewart of Largs), and the section on the application of drying oils in the Leather industries has been read and criticised by Mr. H. G. Crockett (Editor of the *Leather World*). The section on drying oils as electric insulators has been read by Mr. H. Armistead (Rees Roturbo Manufacturing Co.). The authors wish to express their great obligation to these three gentlemen for their

valuable criticisms. The authors' thanks are due to Messrs. Mander Bros., Ltd., and to Messrs. Storry, Smithson and Co., Ltd. for permission to publish this book: to Messrs. Rose, Downs and Thompson, Ltd., and to Messrs. Scott, Ltd., for nine drawings of plant, and to the British Engineering Standards Association for permission to reproduce the details of several specifications. To Mr. J. A. F. Wilkinson the authors wish to express their gratitude for his useful criticism of the manuscript and for his careful correction of the proofs. Whenever necessary the abstracts of the Society of Chemical Industry are quoted for References to foreign papers, which may be difficult to obtain.

R. S. M.

H. R. W.

October 1925.

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THE CHEMISTRY OF DRYING OILS

HISTORICAL AND INTRODUCTORY

It is surprising that the drying properties of linseed oil were unknown to the Egyptians, who were fully acquainted with the value of the textile properties of the linen fibre. Possibly the well-known medicinal application was in common use before the oil was adopted as a medium for pigments. The varnishes used by the Egyptians were of the alcohol-soluble group, and were probably of the soft or balsam-like variety, which required no medium for their application, melting at low temperatures, so that they were sufficiently fluid when applied hot. The Greeks and Romans used wood pitch as a protection for ships' timbers, and melted wax was employed as a medium for pigments, which were mixed with it (A. P. Laurie, private communication). The first mention of the use of oil in painting is by Ludius (an encaustic painter of the Augustan age), who mixed oil with the wax at the burning in of his encaustic paints. Vitruvius, of the same period, used a varnish to prevent vermilion darkening in outdoor work. This varnish consisted of Punic wax (probably beeswax) melted on the fire and tempered with a little oil, then laid on with a brush and driven in by the heat of a portable stove. Dioscorides (time of Antony and Cleopatra, or rather later) describes the beating of vegetable oils into froth, their bleaching by sunlight and their power of dissolving resins. Mention is made of poppy oil only and not linseed oil, and it is not until the time of Pliny that linseed oil (for poultices) and nut oil are specially mentioned, and although Pliny in his "Natural History" repeats that every resin can be dissolved in oils, yet no reference is made to the use of these oils by painters nor (as in the case of gum and size) to their drying properties. Cornelius Celsus (time of Tiberius) writes of red lead as a drier for oil, not for artistic, but for medicinal purposes. By Lucanus (time of Nero) mention is made of the use of oil, in conjunction with balsams, for improving the working of colours for paints. In Galen (A.D. 131—230) nut, hempseed and linseed oils are specifically mentioned as drying oils, which can be coagulated by the use of litharge, white lead and umber. Again in the fourth century a medical writer, Marcellus, repeats Galen's statements. The value of the drying oils to the painter is put forward by the physician Aetius (A.D. 540), of Amida in Mesopotamia, who writes of linseed oil, castor oil and nut oil as being prized in the arts for their drying properties. He also mentions their use to gilders and encaustic painters, due to their protective properties when used as varnishes. In the Lucca manuscript

of the eighth century the first mention is made of oil-resin varnishes as protectives for pictures, and the addition of a staining yellow colour was shown to give to tin a gold-like appearance. That linseed oil could be mixed with pigments without the use of wax was a gradual discovery. In the *Schedula "Diversarium Artium"* of Theophilus (eleventh to twelfth centuries) the use of linseed, olive, walnut and poppy-seed oil in painting and in varnishes is stated, but Theophilus knew of no means of purifying or refining the oils, nor how the drying could be accelerated by the addition of driers. He complains of the very slow setting of the films and the necessity of drying them in the sun. In the writings of Eraclius and Petrus of St. Audemar (St. Omer), twelfth to thirteenth centuries, methods are given for the extraction and refining of oil, by addition of a small quantity of lime, followed by heating and continual skimming. The latter author mentions the use of white lead (ceruse) as a drier, and the bleaching of oil in the sun with frequent agitation. There is evidence that such oil was used rather for decorative purposes than for pictures. The protective value of drying oils, as well as the freedom of working conferred by their presence as media for paints, was recognised in England, France and in Germany in the thirteenth and fourteenth centuries, and no doubt influenced the Northern artists to use them as media for their colours. In Italy it was an age of tempera artists' colours, and it was not until van Eyck's marvellous paintings were seen there that the value of drying oils was appreciated by the Southern artists. Nevertheless very early Byzantine paintings in the Cologne Gallery appear to have been painted in oil, though they are coarse in execution, and would not compare with the smooth finish of the Italian egg tempera. Records of the use of oil for decorative paints are to be found at Ely (fourteenth century), at Canterbury (thirteenth century), in the Painted Chamber at Westminster, and in St. Stephen's Chapel. Large quantities of varnish and oil were employed (thirteenth century), the oil and white lead being ground together, and in the case of several pigments an admixture of some resin was incorporated with the oil. There are records at Bruges of painting in oil medium done in the chapel of the Town Hall at Damme in 1351. It seems to have been the custom to select for each pigment its own special tempera, *e.g.*, ultramarine would be worked in tempera, whereas the rest of the picture might be painted in oil.

In 1388 a manuscript by Johann Alcherius gives a recipe for resin oil varnish in which the fluid is spread with the fingers over the dry painting. In the Strasbourg manuscript (beginning of

fifteenth century) there is evidence of a fuller knowledge of the behaviour of drying oils. The manuscript is written by a master from Lübeck and a master from Kolmar, and was of the time of van Eyck and Cennini. Directions are given for the mixing of varnishes with artists' colours, although these varnishes are quite different from the oil varnishes of to-day, as turpentine was unknown and the resins were of the oleoresin class, *e.g.*, Venice turpentine or Burgundy pitch rosin (*pica greca* or *gloriat*), sandarac from Berenice (varnish) and mastic. Walnut, linseed and hempseed oils were employed, and they were refined, and driers were incorporated therewith. The oil was boiled with pumice stone and calcined bones and skimmed. One ounce of white copperas was added to a quart of oil, which was then put in the sun for four days. Such an oil would be bright, clear and pale; moreover, it would dry quicker than ordinary linseed oil, by virtue of the manganese content of the copperas. The function of manganese as a drier was not recognised until the early part of the last century, when Faraday pointed out its value on purely theoretical grounds. No similar treatment of the linseed oil was known in Italy until much later. Cennino Cennini's method for making linseed oil, fit for tempering colours and also for mordants, by boiling over the fire, produced an oil thickened by heat with a reduction of half its bulk. When the oil was required as a mordant for attaching gold leaf, to each pint of such thickened oil 1 oz. of *vernice liquida* was added (finished varnish, *vernice* alone would indicate sandarac). Such an oil would resemble lithographic oil, being slow drying and deep yellow in colour. Cennini states: "When you have prepared this oil (which is also cooked in another way, better for painting, but not for mordants, for which it must be done on the fire, that is, cooked), take your linseed oil and in the summer time put it in a basin of bronze or copper. In August (*quando è il sole leone*) place it in the sun; and if you keep it there till it is half wasted, it will be exactly right for mixing with colours. And you must know that in Florence I have found the finest and best there can be."

Oil prepared by this method would have much better drying properties, but its durability would be inferior to that of the cooked oil.

According to Vasari (1524—1574) in his "Lives of the Artists," the mode of painting in tempera, which had been adopted by Cimabue about the year 1250 and followed by Giotto, still continued to be the only method for painting on wood and cloth. The disadvantages of the medium as to application of the pigment were admitted, and the advent of van Eyck's pictures into Italy con-

vinced the Italian artists of the value of the oil medium. It is out of place here to attempt to discuss the secret of van Eyck's effects. Whether he used oil alone or added a varnish to his oil medium or worked with an oil-albumen-emulsion is still undecided. Nevertheless it must be admitted that van Eyck was the best of the exponents of the new oil medium, but the method of his technique is probably lost, because later artists of his school were unable to reproduce it. The introduction of varnish into the oil medium is keenly debated. According to Vasari and others in the sixteenth and seventeenth centuries there was no special medium beyond ordinary oil [walnut, which does not yellow with time (Vasari), poppy seed and linseed]. Where varnish happened to be introduced it was more by accident than by a definite plan, whereas, on the other hand, the finished pictures were in most cases varnished. Nevertheless Vasari states that in 1515 Leonardo da Vinci required oils and resins for a special varnish for his pictures.

In the *Hermeneia*, or "Guide to Painting," of Mount Athos, [probably of the sixteenth or seventeenth century, but describing much older methods dating from the eleventh or twelfth century,] egg was used to mix with the colours, although linseed oil and soap were components of the plaster priming in the scheme for decorated chancel screens. The vehicle for icon painting in Russia, according to the Podlinnik, is egg yolk with a final coating of boiled oil, this being the cause of the darkening of the old pictures. Egg was used instead of oil, which was considered to be a production of the hand of man and unworthy of taking part in the representation of the Divinity ("Iconographie Sacrée en Russie," *Revue Archéologique*, vol. vii).

With the adoption of linseed, poppy-seed and walnut oils as media by the Italians, further reference to artists' colours is unnecessary, until the discussion on the cause of the yellowing of oil films and the cracking of paints. In historical sequence, the introduction of turpentine as a thinning medium for varnishes (Alberti of Magdeburg, 1750) is an important advance in the application of drying oils, but there is little to record until the great advance of chemistry in the beginning or middle of the last century. The industry was entirely in the hands of craftsmen, who would sample linseed oil by its taste and decide its drying power by treatment with arbitrary amounts of metallic driers. The craftsmen, of whom the coach-painters were the most skilled, were formerly instructors of the artists in technique, and the secrets of satisfactory selection of media and pigments are still largely in their hands. Even now our knowledge of the drying process is inadequate, although the rate of

oxidation of oils has been carefully studied; but knowledge of the factors of coagulation is scanty. The conditions of gelation of substances in non-aqueous media is especially obscure. In the use of the metallic catalysts there has been little advance, and the introduction of cobalt is the only novelty, although several other metals, such as cerium and vanadium, have been put forward for consideration. The oxidation rate is affected by the presence of small quantities of apparently inactive substances, some accelerating, *e.g.*, salicylic acid, and some retarding. The gelation of the oxidised product is dependent, not only on the presence of ethenoid linkages, but also on the presence of the glyceryl grouping. Reference will be made later to these problems. The defects of linseed oil are generally admitted, and users are always eager to experiment with other drying oils obtainable in large quantity and at a reasonable price. A drying oil with a low water penetration and small water absorbing power, yielding a tough film and not reacting chemically with pigments, is much desired. Films should have a permanence in the air, so that the lustre and plane character of the surface will be maintained. The general protective and adhesive properties of all drying oil films leave much to be desired. The improved facilities for obtaining forms of soluble cellulose esters have recently made consideration of this material worthy of attention.* Few new drying oils have been adopted in Europe and America within the last fifty years. The most popular is the oil from certain species of *Aleurites*, viz. China wood oil or tung oil, which has been used as a protective coating in China and Japan for centuries. The cultivation of the tree in America and in British Possessions is being watched with interest. Nevertheless there are difficulties in the adoption of the oil for usual processes, which have only so far been overcome by blending with linseed oil. Soya-bean oil, since the Russo-Japanese War, has been on trial. Its inferior drying powers render its use alone, unblended with linseed oil, of small value.

The experience with Para rubber-seed oil is especially disappointing. Varieties of *Aleurites* yield oils, *e.g.*, lumbang oil, which are worthy of consideration, especially when blended with tung oil. Perilla oil from China is promising, but the quantity is limited. In America it is easily absorbed whenever it comes into the market. Chia oil and Oiticaca oil have been proposed, but in the former case the supply is restricted and in the latter case the difficulties of extraction of the oil from the seed have not been satisfactorily overcome. Linseed oil, in spite of its emulsifying properties, will still retain its position of greatest popularity for a long time.

* F. Sproxtton: "Cellulose Ester Varnishes," 1925 (Ernest Benn, Ltd.).

CHAPTER I

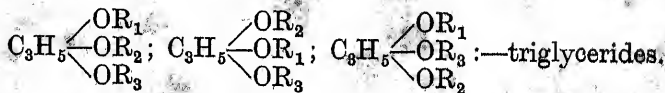
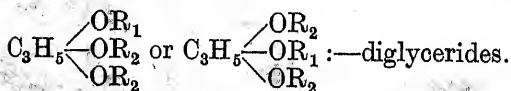
DRYING OILS AND THEIR COMPONENT ACIDS

AN oil which, without loss in weight, slowly sets on exposure to the air to a solid, is classed as a drying oil. The drying is at first accompanied by a gain in weight, so that the loss due to volatile components or decomposition products is less than the gain due to interaction with, or absorption of, one of the components of the atmosphere in which the oil is placed. Such an oil dries in air by combination with oxygen, but drying is possible in any other atmosphere which allows of combination with the gaseous medium and coagulation of the product, so that it is advisable to mention the medium in which the exposure occurs. According to Amer. Soc. Testing Materials, Report of 1922, a drying oil is defined as an oil which possesses to a marked degree the property of readily taking up oxygen from the air and changing to a relatively hard, tough, elastic substance when exposed in a thin film. A semi-drying oil possesses the characteristics of a drying oil, but to a less degree. There is no definite line of demarcation between drying and semi-drying oils. A non-drying oil does not possess to a perceptible degree the power to take up oxygen from the air and to lose its liquid characteristics. The hardening of oils, by reduction in hydrogen to produce a solid fat, is comparable in some respects to the oxidation of a drying oil in air, but the process is simpler in character because the product of the reaction, viz. the solid fat, undergoes no subsequent change such as occurs in the oxidation products of a drying oil.

The rate of setting of an oil film in air is connected with the absorption of oxygen, but it is not dependent on the amount of oxygen which the oil can absorb, because some drying oils set more rapidly than others, although their oxygen absorption is lower. The rate of drying is also dependent on the nature of accelerating catalysts, as well as on temperature, light and hygrometric conditions.

Special reference must be made to the important influence of the glyceryl grouping in connection with the setting power of a drying oil, which is its most important property as a paint or varnish component.

The vegetable drying oils are mixed glycerides of saturated and unsaturated acids, the proportions of which vary with the maturity of the seed.



In the formation of linseed oil in the seed, the proportion of saturated fats present diminishes with maturity (J. V. Eyre), so that, in the growing seed, a change is taking place whereby a special oxidation process is occurring which as yet has not been imitated in the laboratory.¹

Days after flowering.	Oil in dry seeds. %.	Iodine value of oil.
10	2.5	114
14	15.1	119
17	31.1	127
23	37.0	143
35	39.0	180
51	36.3	190

A number of mixed triglycerides of saturated and unsaturated acids have been prepared by the action of anhydrides of unsaturated acids on saturated glycerides, *e.g.*, $\alpha\beta$ -dipalmitin with linolic anhydride yield α -linolo- $\beta\gamma$ -dipalmitin $\left(\text{C}_3\text{H}_5 \begin{matrix} \text{OC}_{18}\text{H}_{31}\text{O} \\ \text{OC}_{16}\text{H}_{31}\text{O} \\ \text{OC}_{16}\text{H}_{31}\text{O} \end{matrix} \right)$.²

Glycerides are hydrolysed by the enzyme lipase, but how far lipase will act toward the three isomeric glycerides just shown is unknown. From C. W. Moore's results, the action of lipase is not affected by the nature of the fatty acid radicle, except in so far as this may have a secondary influence in affecting the nature of the emulsion between enzyme and glyceride. Earlier work by Kastle³ indicated that lipase was sensitive to certain fatty acids, and consequently the esters of all fatty acids were not acted on alike. The hydrolytic enzyme in the castor oil plant acts best in an acid medium of *N*/60- and *N*/100-concentration. In connection with the hydrolysing action of enzymes, a reverse action has been noticed with the enzyme from pig's liver whereby acid and alcohol have reacted to produce an ester, but S. Fokin⁴ was unable to form glycerides from glycerol and fatty acids in the presence of the castor oil-seed enzyme.

The importance of the dependence of the physical properties of a fat on the nature of the glycerides of which it is composed cannot be neglected in the general consideration of drying oils. Two fats may contain the same acid radicle in much the same proportion and yet appear very different in texture, melting point, etc.—factors which are of the greatest importance in their technical application. Although analyses of cacao butter and of South American mutton

tallow show that the percentage of fatty acids obtained from them is nearly the same, yet the two fats are entirely different :—¹

	Cacao butter.	Mutton tallow.
Myristic acid	0	1.5
Palmitic acid	23.2	21.0
Stearic acid	33.6	30.0
Oleic acid	41.8	43.0
Linolic acid	1.4	5.0

The differences of flow of paint and varnish mixings, containing drying and semi-drying oils with almost the same chemical composition, will be familiar to many. The mixed glycerides identified in linseed oil have their like in many oils and fats, *e.g.*, beef fat contains distearopalmitin and dipalmitostearin (Dekker), whereas Amberger and Wiesehan have isolated from lard the following mixed glycerides; β -palmito- $\alpha\gamma$ -distearin; β -stearo- $\alpha\gamma$ -dipalmitin; α -oleo- $\beta\gamma$ -distearin; α -palmito- $\beta\gamma$ -diolein; β -oleo- α -palmito- γ -stearin. A. Bömer and K. Schneider have identified in palm kernel oil, caprylmýristo-olein, m. p. 14°; * myristodilaurin, m. p. 33°; laurodimyristin, m. p. 40°; palmitodimyristin, m. p. 45°, and myristodipalmitin, m. p. 51°. ⁵

It is evident that the consideration of the composition of the mixed glycerides in drying oils is of importance in connection with their gelatinisation, especially in such a complex oil as linseed oil. In the opinion of the writers it is doubtful whether linseed oil, composed of a mixture of glycerides as given by the analysis, would have the same properties as that extracted from the seed. No attempt has been made to synthesise a drying oil from its components. The synthesis of mixed glycerides is by no means easy, as it is complicated by the possibility of internal rearrangement and the wandering of acyl groups in the molecule. A summary of the progress made in the synthesis of mixed glycerides is to be found in the paper by E. F. Armstrong and J. Allan.¹

A method for their preparation must be of such a nature that the three hydroxyl groups of the glycerol can be so differentiated that it is possible to treat them differently at the individual stages of the process; the starting material must be such that two of three groups in the glycerol are at first masked and are uncovered only in the further course of the synthesis, and then only successively.

* Unless otherwise stated, all temperatures are expressed on the Centigrade scale.

A substance fulfilling these requirements is the compound 2-phenyl-5-hydroxymethyloxazolidine, $\text{OH}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{NH}$
 $\text{O}\text{---}\text{CHC}_6\text{H}_5$, which con-

tains one alcohol group. A second alcohol group is produced by the action of acids whereby the compound is hydrolysed to benzaldehyde and aminopropylene glycol, $\text{OH}\cdot\text{CH}_2\cdot\text{CHOH}\cdot\text{CH}_2\cdot\text{NH}_2$, and finally a third alcohol group is produced by treating the ester of the last compound with nitrous acid.

The mixed glycerides of the saturated and unsaturated acids are worthy of further attention. The differences between drying oils such as perilla and linseed may be due, not merely to the higher iodine value of the former, indicating a higher percentage of unsaturated acids, but the nature of the component unsaturated mixed glycerides may also be a factor of importance. H. Toms⁶ states that there are indications that the amount of the most unsaturated glyceride in linseed oil is a constant proportion of the total unsaturated compounds present.

In linseed oil, the following mixed triglycerides have been identified and isolated in the form of bromo-derivatives; (a) dilinolenylmonolinolyl glyceride, $\text{C}_3\text{H}_5(\text{OL}_2)_2\text{OL}_1$ (L_2 = linolenyl, L_1 = linolyl), 25 per cent. of the trilinolic glyceride or an oleic-linolenic glyceride; (b) dioleopalmitin (0.6 per cent. of the oil).⁷ In China wood oil the glycerides present, other than that of elæostearic acid, are few in number.⁸ Replacement of the glyceryl grouping by the ethyl or methyl group has no influence upon the amount of oxygen absorbed on exposure. The effect on the setting or drying of the replacement of glyceryl by an ethyl or a methyl group is profound. The following graph shows the rate of absorption of oxygen by linseed and China wood oil compared with that of the ethyl and methyl esters. The ethyl and methyl esters remain fluid on oxidation, whereas linseed and China wood oils set to a solid film (Fig. 1). The function of the glyceryl grouping has not been satisfactorily explained, and it will be advisable to present later what evidence is available.

The property of "drying" in the case of vegetable oils derived from unsaturated acids, containing up to 18 carbon atoms in open chain, would appear to be associated with esters containing the glyceryl radicle. The majority are glyceryl esters of the open-chain series of unsaturated acids, containing more than one doubly-linked pair of carbon atoms. In the case of animal drying oils, many are esters of acids containing from 14 up to 24 carbon atoms (in whale oil). In menhaden oil, on careful distillation of the methyl esters obtained therefrom, acids containing 14, 16, 18, 20

and 22 carbon atoms have been isolated, and one fraction of the methyl esters was found to be practically pure methyl clupanodionate ($C_{22}H_{34}O_2$, clupanodonic acid)^{8, 9, 10}

In the fish-liver oils there is an extraordinary series, with high iodine values, high and low saponification values and containing a large proportion of unsaponifiable matter.¹¹

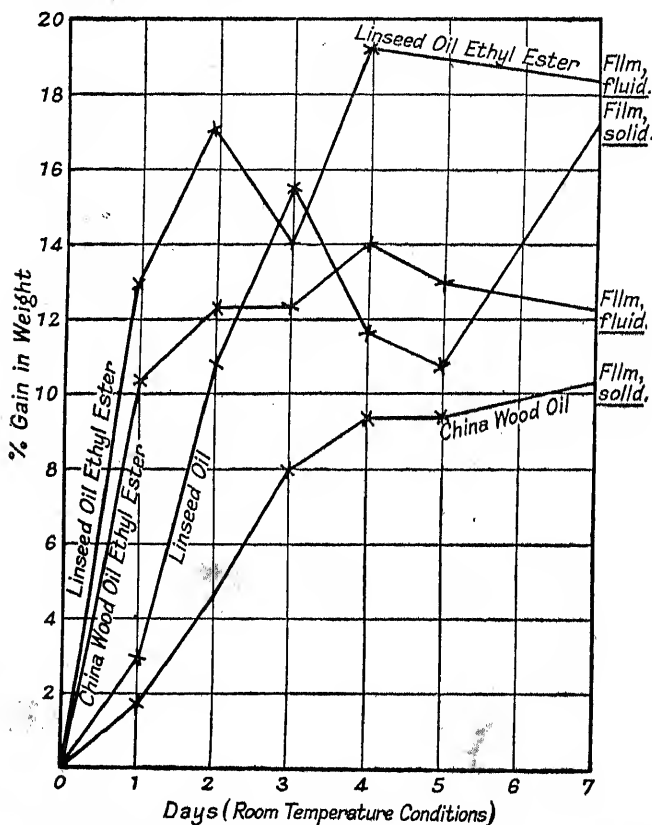
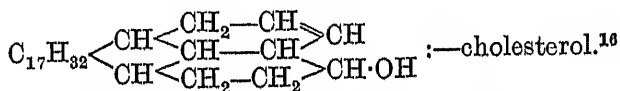


FIG. 1.—Comparison of Rate of Gain in Weight on Oxidation of Ethyl and Glyceryl Esters of Drying Oil Acids.

	Sap. value.	Iodine value.	Refractive index 20°.	Unsapon. matter. %.	Insol. bromides from fatty acids. %.
Sun fish	180.2	151.8	1.4786	3.2	43.5
Common ray	182.7	183.7	1.4825	3.15	60.2
Basking shark ...	102.45	178.3	1.4773	41.92	—
Shark (Moroccan)	22.5	358	—	89.1	—

The unsaponifiable matter contains hydrocarbons, *e.g.*, spinacene, $C_{29}H_{48}$,¹² and squalene, $C_{30}H_{50}$, which are unsaturated hydrocarbons, and on exposure to air form a tough skin similar to that given by linseed oil. The presence of unsaturated and saturated hydrocarbons in fatty oils, cf. iso-octadecane, $C_{18}H_{38}$, occurring in liver oils containing squalene (*J.*, 1923, 42, 840A), is probably of much more frequent occurrence than has hitherto been supposed, and there can be no doubt that unsaponifiable matter other than cholesterol, phytosterol and similar alcohols, often consists mainly of hydrocarbons.¹⁴ The alcohols referred to above, occurring in the unsaponifiable part of the oil, are probably of a terpene nature, *e.g.*, cholesterol ($C_{27}H_{45}OH$) occurs in animal fats, and sitosterol (phytosterol) ($C_{27}H_{45}OH$) and dihydrositosterol ($C_{27}H_{47}OH$), occur in vegetable fats.¹⁵ In the endosperm of wheat the saturated and unsaturated sitosterols occur together.¹



Y. Toyama¹⁷ has identified alcohols in a number of fish and shark oils, *e.g.*, selacyl alcohol, which on hydrogenation passes into butyl alcohol and chimyl alcohol, $C_{19}H_{40}O_3$. The following formula has been suggested for selacyl alcohol, $CH_3(CH_2)_7 \cdot CH:CH \cdot C_{11}H_{21}O(OH)_2$, an unsaturated alcohol like cholesterol.

Toyama has also identified olein alcohol, $C_{18}H_{31}O$, which is a reduction product of oleic acid. The occurrence of hydrocarbons and alcohols associated with glyceryl esters is an interesting fact to be considered in a discussion on the formation of vegetable and animal oils and fats. The fats obtained from whales are divided into two classes, (a) glycerides from *Balaena* blubber, (b) sperm oils consisting of fatty acid esters of monohydric alcohols, *e.g.*, spermaceti, is almost pure cetyl palmitate ($C_{16}H_{34}O \cdot C_{16}H_{33}O$). The unsaturated vegetable fats of chaulmoogra (*Taraktogenos Kurzii*) and hydnocarpus seeds are glycerides of unsaturated closed ring acids. These fats are of no interest in the paint and varnish industry, but have pharmaceutical value, especially the fat from hydnocarpus seeds, in the treatment of leprosy, and exert an inhibiting action on the tubercle bacillus. The fatty acids from chaulmoogra contain a crystalline acid, $C_{18}H_{32}O_2$, m. p. 68° , which is chaulmoogric acid. The oils from hydnocarpus contain C_{16} acids, which, like chaulmoogric acids, are optically active and are unsaturated ring compounds. Hydnocarpic acid has the formula $C_{16}H_{28}O_2$, and can be

separated from chaulmoogric acid by fractionation of the methyl esters. The existence of a vegetable drying oil containing less than 16 carbon atoms in the form of isanic acid, $C_{13}H_{19}COOH$ ($C_nH_{2n-7}COOH$), m. p. 41° , is doubtful. It is stated to be obtained from an oil of the seeds of T'sano (*Oleaceae*) in the French Congo. It is said to absorb oxygen to give a rose-coloured substance insoluble in ether (J., 1896, 660).

Vegetable drying oils do not show the elaidin reaction, whereas non-drying unsaturated oils on treatment with nitrous acid yield solid isomerides (elaidins), e.g., olive oil gives solid isomeric tri-elaidin, and trierucin from tropæolum oil gives a solid tribrassinidin. Not all the acids or fats of the oleic acid series show the elaidin reaction, e.g., rape oil containing rapic acid ($C_{18}H_{34}O_2$) gives no elaidin with nitrous acid.

In addition to the unsaponifiable matter mentioned under sitosterol, vegetable drying oils contain colouring matter which may consist of chlorophyll, carotin and xanthophyll, concerning the former of which I. M. Heilbron has summarised the present state of knowledge.¹⁸ An interesting statement by J. V. Eyre on the colouring matter of drying oils is stimulating to further investigation.

Linseed oil extracted, or pressed from immature seed is always of a green chlorophyll colour; it is only after the bulk of the oil has been laid down in the seed that it loses its bright green colour, and, as ripening proceeds, both seed and oil assume a yellow colour. It seems possible that what is present in the leaf of the plant in this case may be present in the seed, and that carotin (hydrocarbon, $C_{40}H_{56}$, Willstätter), and xanthophyll (an oxidation product of carotin, $C_{40}H_{56}O_2$, Willstätter), which are orange and yellow respectively and occur with chlorophyll in the leaf, may occur also in the seed. On chlorophyll disappearing during ripening of the seed, carotin and xanthophyll may remain and give colour to the oil. Both these substances are unsaturated in character and it may be that carotin acts as an oxygen carrier, being itself finally converted into xanthophyll. (J. V. Eyre, private communication.)

Another component of vegetable drying oils is "mucilage or spawn," which is partly albuminous and partly pectinous. It is derived from the cell substance of the seed, pressed out with the oil. In the same category mention must be made of phosphatides (phospholipins), a large group of naturally occurring mixed glycerides, containing as a rule two fatty acid radicles and one radicle of phosphoric acid. Their chemical composition may be represented by the general formula $C_3H_5(OR)(OR')(O \cdot PO) \cdot OH(OB)$,

where B stands for a monoamino-base. The details respecting mucilage and its components will be dealt with in a later chapter.

It has been pointed out that in any vegetable drying oil the acidity and degree of unsaturation of the oil vary with the age of the seed. In fish oils, the amount of the unsaponifiable matter varies with the season. From stearic acid to linolenic acid glycerides there are gradations through non-drying, semi-drying to drying oils, *e.g.*, the glycerides of the oleic, linolic and linolenic acids series. In the fish oils, the gradations are marked, more especially in the variation of the number of carbon atoms present in each acid, and reference has been made to a series of 14 to 22 atoms of carbon present in menhaden oil.

It will not be out of place here to refer to the variation in the odour of oil which is associated with the term "rancidity."

The rancidity of oil is accompanied by an increase in acidity, due to the action of moisture in the presence of soluble ferments, but the cause of rancidity is to be looked for in the oxidation of the free fatty acids, intensified by exposure to light. It has been stated that the more saturated acids the fat contains, the less liable is it to become rancid; cacao butter is rarely found to undergo this change; also that the higher the percentage of unsaturated glycerides in a fat the less will be its liability to turn rancid. Oleic acid is considered to be the main constituent in fats and oils concerned in the production of tallowness and rancidity, and the olfactory sense gives no true criterion of how highly oxidised a fat or oil may be.¹⁹ W. C. Powick suggests that the odour of rancid fat is in part due to the formation of nonylic acid.²⁰ He examined a large number of decomposition products of fat, with the object of determining those responsible for the odour and for manifesting the Kreis reaction. The colour developed in the Kreis test for rancidity was spectroscopically identical with that obtained by applying the test to a mixture of acrolein and hydrogen peroxide. The reacting compound is probably an epihydrin aldehyde,

$$\text{O} < \begin{array}{c} \text{CH}_2 \\ \text{CH} \cdot \text{CHO} \end{array} \quad ^{21}$$
 It is considered likely that a derivative of this

compound, *e.g.*, the acetal, exists in rancid fats, and is decomposed during the addition of hydrochloric acid in the Kreis test.²² E. Boedtker²³ states that the rancidity of cocoa-nut oil is due to the presence of volatile higher ketones.²⁴ W. Rhys-Davies²⁵ has examined the rancidity of olive oil on wood fibres and has shown that the high acidity does not cause rancidity, which is produced from oxidised oil and is caused by an enzyme belonging to the oxydases,

which Rhys-Davies has named "rancidase." In rancid cotton oil 0.6 per cent. free and 9.8 per cent. combined azelaic acid have been found.²⁶ From the evidence submitted it would appear that rancidity is due to the formation of volatile oxidation products, some acidic, some aldehydic. The best known instance of rancidity in a drying oil is furnished by China wood oil, which gives an odour of valerianic aldehyde. The first stage is probably the formation, under the influence of light and air, of a peroxide at the ethenoid linkage. The peroxide decomposes in the presence of water, giving an ethylene oxide derivative and hydrogen peroxide. At the same time, the peroxide may be decomposed to give aldehydes of rancid odour. The presence of hydrogen peroxide in strongly rancid fats has been confirmed.²⁷ It is worthy of mention that a film of wood oil, dried in air on glass to give a matt, corrugated solid film, has a much stronger odour than a film of the same oil dried in a moisture-saturated atmosphere, the latter film being clear, probably due to the increase in volume caused by water absorbed by the unoxidised oil, in contrast to the microscopically corrugated film of the former.

The Component Acids of Drying Oils.

In any description of the properties of oils and fats it is advisable to have a knowledge of the properties of the component acids, beginning with the saturated acids and passing to the unsaturated members. In the case of the drying oils, the lowest saturated acid occurring as glyceride is *Myristic Acid*, $C_{14}H_{28}O_2$, which is stated to occur in small quantities in linseed oil,²⁸ as well as in cod-liver oil. It may be obtained by fractionally distilling under reduced pressure the acids produced by the hydrolysis of nutmeg butter, with subsequent repeated recrystallisation from alcohol. Myristic acid is a crystalline solid, m. p. 53.8° , b. p. at 15 mm., 196.5° and $121-122^\circ$ *in vacuo*. It is volatile in superheated steam at 165° (38 mm.), the distillate giving a 65.7 per cent. yield of myristic acid. The ammonium, lithium, barium, magnesium and lead salts have received attention, the lead salt being more readily soluble in ether than that of palmitic acid.

Palmitic Acid, $C_{16}H_{32}O_2$, is an important member of the saturated acids series, occurring in vegetable drying oils, especially in association with stearic acid. In the deposits obtained from lead drying oils, the two acids are easily identified, although their quantitative separation is difficult.²⁹ Fachini and Dorta make use of the differences in solubility in acetone of the alkali salts of the saturated acids (solids) and of the unsaturated acids (liquids). For the paint

and varnish manufacturer, the distinctive properties of palmitic acid compared with stearic acid are of little importance and the details concerning them can be found in the larger text-books of organic chemistry. Lead palmitate is almost insoluble in ether and in petroleum ether.

Stearic Acid, $C_{18}H_{36}O_2$, is another component of linseed oil and of many drying oils of the C_{18} open-chain series. The following table gives the melting point of the saturated acids open-chain series, together with their specific gravity and comparative solubilities in alcohol.

	M. p.	S. G.	Solubility in alcohol (grams in 100 @ 20°).		
			Absolute alc.	75% alc.	50% alc.
Myristic acid, $C_{14}H_{28}O_2$	53·8°	0·8584 60°/4°	With difficulty.	—	—
Palmitic „ $C_{16}H_{32}O_2$	62·6	0·8412 80°/4°	9·2	0·43	0·9
Stearic „ $C_{18}H_{36}O_2$	69	0·8386 80°/4°	20	—	0·08
Arachidic „ $C_{20}H_{40}O_2$	75	—	0·045 (90% alc.)	—	—
Daturic „ $(C_{17}H_{34}O_2)$	59·5	0·8532 60°	13·4 @ 21°	—	—
Behenic „ $(C_{22}H_{44}O_2)$	83–84	—	0·102 @ 17°	—	—

The saturated acids themselves call for little comment. They all contain a straight chain of carbon atoms and no isomerism is possible; they crystallise in one form only, the crystal unit being composed of two molecules arranged end to end with the carboxyl groups adjacent to each other. It is of interest that the synthetic acids containing an odd number of carbon atoms in this series are many of them enantiomorphic, *i.e.*, they have two melting points and crystallise in two forms. This is ascribed by Garner and Randall to alternative methods of arrangement of the two molecules of the acid which go to make the crystal unit.³⁰

The existence of acids with an uneven number of carbon atoms in oils and fats is doubted in the case of margaric acid, $C_{17}H_{34}O_2$, but daturic acid ($C_{17}H_{34}O_2$) is stated to exist in datura oil.³¹ Margaric acid has, however, been synthesised from α -hydroxystearic acid, from which, on heating to 270°, margaric aldehyde, $C_{16}H_{32}CHO$, was obtained and oxidised to margaric acid.³²

The metallic stearates, especially aluminium, copper and zinc stearates, are of interest to the paint and varnish manufacturer.³³ The potassium and sodium stearates are of more concern to the soapmaker. The aluminium and zinc stearates are in demand for

When stearic acid is heated with cast-iron filings at 280° the corresponding ketone, $(C_{17}H_{35})_2CO$, stearone, is formed. Similar ketones, cf. oleone, $(C_{17}H_{33})_2CO$, m. p. 59° , from oleic acid, are produced by the same general treatment of the higher fatty acids.³⁷

Arachidic acid ($C_{20}H_{40}O_2$) occurs as a glyceride in a number of non-drying oils and in small quantities in many semi-drying oils, e.g., arachis oil, rape oil, soya-bean oil, possibly linseed oil, etc. It may also be prepared from erucic acid, $C_{22}H_{43}O_2$, of rape-seed oil through fusion with potassium hydroxide.³³

Oleic Acid Series. $C_nH_{2n-2}O_2$.

The unsaturated acids in vegetable fats are almost wholly C_{18} acids and contain not more than three ethenoid linkages.

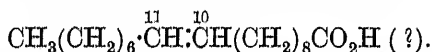
Oleic acid, which is the most important member of the series, has the formula $C_{18}H_{34}O_2$, but acids with a smaller number of carbon atoms occur in fish oils. Myristoleic acid, $C_{14}H_{26}O_2$ (Tsuji-moto), is a constituent of sperm and dolphin oils, and is stated to have the constitutional formula $CH_3(CH_2)_7\overset{6}{CH}:\overset{5}{CH}(CH_2)_3CO_2H$. Palmitoleic acid, $C_{16}H_{30}O_2$, occurs to the amount of 17 per cent. in whale oil, from which it can be separated in almost a pure state, and it is also found in skin grease to the amount of 12 per cent. It gives an iso-acid (m. p. $21-22^{\circ}$) by the elaidin reaction. Its constitutional formula is unknown.

With variation in the position of the ethenoid linkage the isomers of oleic acid are numerous. A characteristic of this series is the occurrence of stereoisomerides of acids with different positions in the ethenoid linkage. The following are the more important isomers of oleic acid:—

Ordinary oleic acid (m. p. $14-16^{\circ}$), 9 : 10 octodecylenic acid,



Iso-oleic acid (m. p. 44°), 10 : 11 octodecylenic acid,



Iso-oleic acid (Moore), 11 : 12 octodecylenic acid,



Iso-oleic acids of unknown constitution are formed during the distillation of stearin or during hydrogenation of oleic acid (Moore).

Petroselenic acid (m. p. $33-34^{\circ}$) (from parsley seed oil), 6 : 7 octodecylenic acid,³⁹



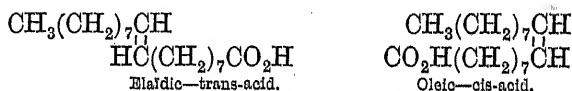
Rapinic acid⁴⁰ occurs in rape oil, is fluid and gives no elaidin modification.

Hepatic oleic acid, identified by Hartley as having the structure 12 : 13 octodecylenic acid, $\text{CH}_3(\text{CH}_2)_4\overset{13}{\text{CH}}:\overset{12}{\text{CH}}(\text{CH}_2)_{10}\text{CO}_2\text{H}$.

Synthetic oleic acid (m. p. 58—59°), 2 : 3 octodecylenic acid, $\text{CH}_3(\text{CH}_2)_{14}\overset{3}{\text{CH}}:\overset{2}{\text{CH}}\cdot\text{CO}_2\text{H}$, prepared from stearic acid.⁴¹

Hepatic oleic acid (liver-lecithin oleic acid) has no elaidin modification.⁴²

Elaidic acid is the solid isomer of oleic acid (m. p. 44·5°) and is produced by the general method of nitrous acid treatment of the normal oleic form. It is regarded as a trans-compound, whereas oleic acid is the cis-product, being the result of enzyme action in the living cells, whilst elaidic acid is not a natural product. Muller and Shearer from X-ray examination regard elaidic acid as a trans-compound.

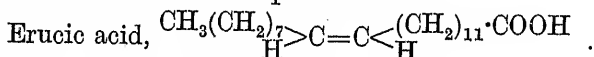


Petroselinic acid has its elaidic form, known as cheiranthic acid, m. p. 30°.

Tarelaïdic acid is the stereoisomer of tariric acid, $\text{C}_{18}\text{H}_{32}\text{O}_2$, which contains a triple carbon linkage, $\text{CH}_3(\text{CH}_2)_{10}\overset{7}{\text{C}}\equiv\overset{6}{\text{C}}(\text{CH}_2)_4\cdot\text{COOH}$.

Iso-oleic acid, 9 : 10, has a similar solid stereoisomer.

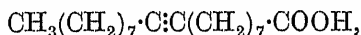
A higher member of the series is erucic acid, $\text{C}_{22}\text{H}_{42}\text{O}_2$, m. p. 34°, which is contained in cruciferous oils, colza oil, in the oil from *Tropæolum majus* and also in cod-liver oil. In properties it resembles oleic acid, giving a lead salt easily soluble in warm ether, and an elaidin form, brassidic acid, m. p. 65°, which is considered to be the trans-modification.⁴³ It absorbs one molecule of ozone, and like oleic acid it forms a perozonide.⁴⁴



Brassidic acid, $\text{CH}_3(\text{CH}_2)_7\text{CH} > \text{C} = \text{C} < \text{CH}_2(\text{CH}_2)_{11}\cdot\text{COOH}$. Its lead salt is with difficulty soluble in warm ether. Hydriodic acid reduces it to behenic acid [in ben (behen oil)],⁴⁵ m. p. 81—82°, $\text{C}_{22}\text{H}_{44}\text{O}_2$, *n*-docosanic acid,⁴⁶ corresponding to a saturated stearic acid. Erucic acid is probably $\text{CH}_3(\text{CH}_2)_7\overset{14}{\text{CH}}:\overset{13}{\text{CH}}(\text{CH}_2)_{11}\cdot\text{COOH}$. Iso-erucic acid, m. p. 54—56°, has been obtained by the action of hydriodic acid on erucic acid with subsequent treatment with alcoholic potash.

Neither oleic (9 : 10) nor isoleic acid (10 : 11) has been synthesised,

although the Report of the Food Investigation Board, 1920, describes attempts in progress, which require the preparation of a number of intermediate substances. No doubt the synthesis will be accomplished and the constitutional formulæ of the acids established; at present they rest on the results of investigations on their decomposition products. The investigations of Baruch⁴⁷ on the decomposition of the oximes obtained from stearolic acid,



and of Harries and Erdmann with Bedford on the decomposition of the ozonides, have met with success, although the constitutional formulæ put forward, for the more unsaturated members of the open-chain series, have been challenged as not representing all the properties of the acid.

Oleic Acid, 9 : 10, or *θ*, *Oleic Acid*, $\text{CH}_3(\text{CH}_2)_7\overset{10}{\text{CH}}:\overset{9}{\text{CH}}(\text{CH}_2)_7\text{COOH}$. —This acid is of interest to the paint and varnish maker as a minor component of linseed oil, poppy-seed oil, soya and China wood oils, and because of the properties of some of its metallic salts. In its pure form it is best prepared from tallow, which does not contain any less saturated acids. The fat is saponified by caustic alkali, and the lead salt precipitated by lead acetate and extracted with ether. The solution of lead oleate in ether is decomposed by hydrochloric acid, and after the removal of the ether, the oleic acid is purified by neutralisation with ammonia and is precipitated as the barium salt by barium chloride. Barium oleate is recrystallised from alcohol, and the acid obtained by decomposing the salt with tartaric or a mineral acid. The oleic acid thus obtained still contains traces of solid acids, and it has been suggested that the ICl compound should be prepared and separated from the saturated acids by an organic solvent, from which the purified compound can be extracted, decomposed by aniline and the pure acid obtained. An attempt to prepare pure oleic acid, by distillation of crude oleic acid under reduced pressure, gave an acid, m. p. 10°, which appeared to contain 20 per cent. of elaidic acid.⁴⁸ Oleic acid melts at 14—16°, and is probably dimorphous. On distillation at the ordinary pressure it is decomposed into acetic, caproic ($\text{C}_6\text{H}_{12}\text{O}_2$), caprylic ($\text{C}_8\text{H}_{16}\text{O}_2$), sebamic acids ($\text{C}_{10}\text{H}_{18}\text{O}_4$), water, hydrocarbons and carbon dioxide, but it can be distilled unchanged in superheated steam at 250°, which is the method of obtaining commercial oleic acid in candle-works. It is insoluble in water, soluble in alcohol and on exposure to air it becomes rancid, giving cēnanthaldehyde ($\text{C}_7\text{H}_{14}\text{O}$), formic, acetic, butyric and cēnanthic acids ($\text{C}_7\text{H}_{14}\text{O}_2$), which are also the

products of the rancidity of olive oil. Oxidation by alkaline permanganate gives 60 per cent. of dihydroxystearic acid



16 per cent. of pelargonic acid ($C_9H_{18}O_2$), and 16 per cent. of oxalic acid. If enough alkali be present to neutralise only the oleic acid used, keto-hydroxystearic acid as well as dihydroxystearic acid are obtained.⁵⁰

The absorption of ozone by unsaturated acids is of great importance in elucidating their structural formulæ. Harries⁵¹ and Molinari⁵² obtained an ozonide, $CH_3 \cdot (CH_2)_7 \underset{O \cdot O \cdot O}{CH-CH} (CH_2)_7 COOH$, which

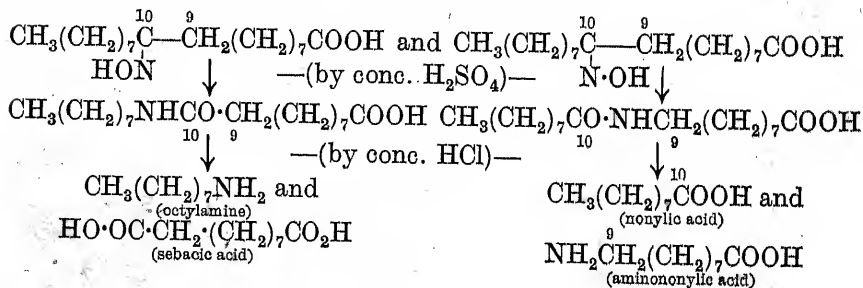
is a yellow oil, easily soluble in benzol and chloroform. Harries maintains that under certain conditions perozonides ($C_{18}H_{34}O_6$ and $C_{18}H_{34}O_7$) can also be obtained. The ozonide is decomposed by water to give nonylaldehyde (I), nonylic acid, the semialdehyde of azelaic acid (II) and azelaic acid (III).



Glacial acetic acid will also bring about the same decomposition, but if an alkali be present, the aldehydes are oxidised to acids by the sodium peroxide formed. The ozonides are saturated substances, which do not decolorise bromine, but they are oxidising agents and liberate iodine from potassium iodide. The position of the ethenoid linkage in the oleic acid molecule is demonstrated by the decomposition of the ozonide, and has been confirmed in another way by Baruch (*loc. cit.*), who transformed oleic acid into dibromostearic acid. This, on treatment with alcoholic potash, gave stearolic acid $[CH_3(CH_2)_7C:C(CH_2)_7COOH]$, and on treatment with concentrated sulphuric acid gave ketostearic acid,



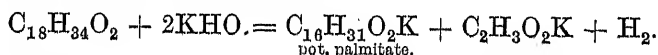
Ketostearic acid forms with hydroxylamine two stereoisomeric oximes, which are decomposed by sulphuric and hydrochloric acids successively, according to the following scheme:—



Therefore the double linkage in the chain lies between the ninth and tenth carbon atoms.

Just as oleic acid unites with 2 atoms of bromine to give dibromostearic acid, so it can be made to unite with 2 atoms of hydrogen, by the well-known Sabatier's process, to give stearic acid, using a nickel catalyst, or at the ordinary temperature by means of colloidal platinum. Oleic acid dissolves in concentrated sulphuric acid to give $C_{18}H_{35}(HSO_4)O_2$, which, on treatment with boiling water, gives hydroxystearic acid $[C_{17}H_{34}(OH)COOH]$, together with an anhydride of that acid.

Fusion with solid potash yields salts of palmitic and acetic acids, as in the case of elaidic acid :—



The oleates of interest to the varnish-maker are (a) lead oleate, m. p. 45—50°, soluble in ether, but not so completely as to allow of satisfactory separation from saturated acids; lead oleate is soluble in petroleum ether and does not occur in lead drying oil bottoms: it may also be used as a drying catalyst in oil varnishes, but it has a tendency to soften the solidified oil films: (b) aluminium oleate is gelatinous, sparingly soluble in ether, petroleum ether and benzene, and is used as an oil thickener: it is insoluble in alcohol; (c) barium oleate is insoluble in water, but soluble in a mixture of benzene and alcohol containing 5 per cent. of 95 per cent. alcohol, from which it can be crystallised on cooling the solution.⁵³

Elaidic Acid.—The action of nitrous acid on oleic acid yields a stereoisomeric crystalline modification whose formula has already been given. Elaidic acid crystallises in plates melting at 44.4° and can be distilled under reduced pressure (b. p. 234°, 15 mm.). In chemical properties it closely resembles oleic acid; on reduction it yields stearic acid; on oxidation the products are a dihydroxystearic acid, $C_{18}H_{34}O_2(OH)_2$, m. p. 99° (33 per cent.); pelargonic acid, $(C_9H_{18}O_2$, nonylic acid) (13—14 per cent.); azelaic acid (26 per cent.); and oxalic acid (15—20 per cent.). The action of fused caustic potash and of concentrated sulphuric acid is similar to what is observed with oleic acid. The barium, lead and silver salts are sparingly soluble in ether.

Linolic Acid Series. $C_nH_{2n-4}O_2$, $n = 18$.

Acids of the Formula $C_{18}H_{32}O_2$.—Four geometrical isomerides are possible for an acid with 18 carbon atoms in this series. Probably more than one linolic acid occurs in animal and vegetable fats,

but whether the isomerism is structural or geometrical cannot be stated. In addition to the acids containing two ethenoid linkages an acid is known containing one triply-linked pair of carbon atoms,

in the form of tariric acid, $\text{CH}_3(\text{CH}_2)_{10}\overset{7}{\text{C}}\overset{6}{\text{C}}(\text{CH}_2)_4\text{COOH}$,⁵⁴ which occurs in the oil from the seed of the Guatemalan "Tariri" and from *Picramnia lindeniana* (to the extent of 20 per cent. of the oil). It melts at 50.5° , absorbs only 4 atoms of bromine and yields stearic acid on reduction. By careful oxidation it yields a diketone acid, $\text{CH}_3(\text{CH}_2)_{10}\text{CO}\cdot\text{CO}(\text{CH}_2)_4\text{COOH}$. Tariric acid is of no interest to the paint and varnish maker. The two most important members of the series are linolic and elæostearic (elæomargaric) acid, which occur as glycerides in a number of oil seeds. Ricinoleic ($\text{C}_{18}\text{H}_{34}\text{O}_3$) and ricinelaïdic ($\text{C}_{18}\text{H}_{34}\text{O}_3$) acids yield on distillation, among other products, two different acids, each with the formula $\text{C}_{18}\text{H}_{32}\text{O}_2$.⁵⁵ The accepted formula for linolic acid is:—²elæostearic

$\text{CH}_3(\text{CH}_2)_4\overset{13}{\text{CH}}\overset{12}{\text{CH}}\overset{10}{\text{CH}_2}\overset{9}{\text{CH}}\overset{7}{\text{CH}}(\text{CH}_2)_7\text{COOH}$ ~~old formula~~
It is shown that there are three conjugated double bonds in linolic oil.

and for elæostearic acid:—

$\text{CH}_3(\text{CH}_2)_3\overset{14}{\text{CH}}\overset{13}{\text{CH}}\overset{10}{\text{CH}_2}\overset{9}{\text{CH}}\overset{7}{\text{CH}}(\text{CH}_2)_7\text{COOH}$.

Linolic Acid.—The glyceride occurs in considerable proportion in drying and semi-drying oils and is most readily obtained from poppy seed, soya bean, maize, cotton seed and sesame oils by brominating the mixed fatty acids, purifying the tetrabromide (m. p. 114°), by recrystallisation from light petroleum and reducing it with zinc and hydrochloric acid in methyl-alcoholic solution. The tetrabromide is easily soluble in ether, alcohol, benzene, chloroform and acetic acid, but it is sparingly soluble in light petroleum, in which the dibromo-oleic acid is easily soluble. The methyl ester of linolic acid is saponified in the cold with alcoholic caustic potash and the acid liberated by dilute hydrochloric acid. Full details for the preparation of the acid are given by Rollett.⁵⁶

The glyceride of linolic acid is also present in a large number of non-drying oils and fats in small quantities, cf. lard, horse fat, etc. A. Eibner^{56A} has detected a linolic acid in castor oil. Linolic acid is a liquid, sp. g. 0.9026 (18°) and boils at $229\text{--}230^\circ$ at 16 mm. It is soluble in alcohol and in ether. No solid isomeride is formed on treatment with nitrous acid. Linolic acid absorbs oxygen from the air, when exposed as a thin film, and is converted within a few days into a solid resinous substance, passing, on further exposure, to a neutral body (a linoxyn) which is insoluble in ether.⁵⁷ Matthes and Bolze obtained from the liquid modification a crystalline tetrabromide,

m. p. 57—58°, by recrystallisation from methyl alcohol.⁵⁸ The tetrabromide is obtained in two forms, one soluble in light petroleum and a liquid, and the second form, melting at 114—115°, is crystallisable from light petroleum. Rollett obtained a 50 per cent. yield of solid tetrabromide and a 50 per cent. yield of the fluid variety, which furnished on reduction an acid yielding a crystalline tetrabromide (m. p. 113—114°), but only to the extent of 26 per cent. of the calculated yield. He concluded that two isomeric bromo-acids were formed in the bromination. Bedford⁵⁹ maintained the existence of two isomeric linolic acids, but the experimental proof was not conclusive.⁶⁰ Telfairic acid ($C_{18}H_{32}O_2$), occurring in Koeme oil, solidifies at 6°, gives a tetrabromide, m. p. 57—58°, and a tetrahydroxystearic acid, m. p. 177°, which suggests that linolic acid may exist in two geometrical modifications. The constitutional formula of telfairic acid is unknown. B. H. Nicolet and H. L. Cox⁶¹ state that only two of the four stereoisomeric forms exist in the linolic acid as usually prepared, viz. *trans-trans-* and *trans-cis-*forms, but the linolic acid examined by them was obtained from the tetrabromide, prepared from cotton-seed oil, and the structure of linolic acid in the above oil has not been definitely proved. According to Eibner, α - and β -linolic acids occur in linseed oil, cf. p. 48.

New evidence, based on the analysis of the products of hydrogenation of cotton-seed, arachis-seed and soya-bean oils, shows the preferential conversion of linolic acid into oleic acid and its isomers.⁶² The constitutional formula as already mentioned is :—



The formula rests on the following evidence: oxidation of linolic acid by potassium permanganate yields sativic acid (tetrahydroxystearic acid, $C_{18}H_{36}O_6$). Rollett (*loc. cit.*) obtained a 40 per cent. yield of a tetrahydroxy-acid (m. p. 155°), which on boiling with light petroleum and recrystallisation from alcohol, gave an acid (m. p. 171—173°). He maintained that two isomeric hydroxy-acids are produced in the oxidation. In the oxidation of a mixture of linolic acid (90 per cent.) and linolenic acid (10 per cent.) very small quantities of volatile acidic oxidation products were obtained, although 27.1 per cent. of oxygen was absorbed; this shows that, in the drying of linseed oil, the volatile acidic products originate from linolenic acid.⁶⁴ Linolic acid is easily reduced to stearic acid ($C_{18}H_{36}O_2$) by hydrogen and a nickel catalyst. The calcium, barium, zinc, copper and lead salts are soluble in ether; barium linolate is soluble in benzene and light petroleum (cf. barium oleate). The

linolates absorb oxygen more readily than does the free acid. The methyl ester is a liquid (b. p. 211—212° at 16 mm.; s. g. 0.886, 18°), and is obtained from the tetrabromide by reduction with zinc and hydrochloric acid in methyl alcohol solution.

Elæostearic (Elæomargaric) Acid, $C_{18}H_{32}O_2$, occurs as the glyceride in two forms in China wood oil (tung oil), together with 10—15 per cent. of olein, which latter includes 2—3 per cent. of fatty acids. M. Nonaka⁶⁵ states that 2½ per cent. stearic acid is also present as glyceride. Wood oil is a case of an almost simple one acid glyceride as compared with the mixed acid glycerides of other oils. The α -acid melts at 48°, whilst the β -acid, which is obtained from the solid β -glyceride,⁶⁶ melts at 71°. Both modifications give the same tetrabromo-acid, m. p. 114—115°, which is not identical with the tetrabromo-acid obtained from linolic acid.⁶⁷ The tetrabromide from either acid yields on reduction only β -elæostearic acid.⁶⁸

M. Ishio⁶⁹ obtained from α -elæostearic acid, by bromination in ether at -15° , a dibromo-acid, m. p. 91°, and by bromination in chloroform solution he obtained the tetrabromide, m. p. 115°. By treatment with alcoholic potassium hydroxide the tetrabromide yields a crystalline dibromide, m. p. 40—40.5°, $C_{18}H_{30}O_2Br_2$ or $C_{18}H_{32}O_2Br_2$.

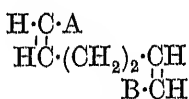
The peculiar drying properties of tung oil must be associated with the orientation of the ethenoid linkages in the molecule of the acid, since it is isomeric with linolic acid, which is present as a glyceride in poppy-seed oil to the amount of 65 per cent.

Linolic acid, $CH_3(CH_2)_4CH:CH(CH_2)_7COOH$.

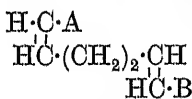
Elæostearic acid, $CH_3(CH_2)_3CH:CH(CH_2)_2CH:CH(CH_2)_7CO_2H$.

The proof of the above formula depends on considerations of the nature of the decomposition products obtained by oxidation with ozone or potassium permanganate. On oxidation with ozone, valeric, $CH_3(CH_2)_3COOH$, azelaic, $COOH(CH_2)_7COOH$, and succinic, $COOHCH_2CH_2COOH$, acids are obtained,⁷⁰ whilst valeric, azelaic acids, together with carbon dioxide, are the products of oxidation when potassium permanganate is employed for the α - or β -acids.⁷¹ The position of the two methylene groups, between the two ethenoid linkages, evidently confers special properties on the acids, especially with reference to the action of light and the production of an elaidin modification. On reduction, stearic acid is obtained, confirming the open-chain arrangement in the molecule. In the description of the two modifications of the acid, it is advisable to consider them together. The α -acid can be separated from the β -acid by fractional

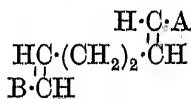
crystallisation from alcohol at 0° , whereby the less soluble β -acid crystallises out first. On exposure of thin layers of the α -acid to the air, the crystals become greasy in $1-1\frac{1}{2}$ hours, semi-fluid in 4—5 days and after 8—10 days a clear yellow syrup is formed; whereas the β -acid appears unchanged after 14 days, after 3 weeks it becomes lumpy and after 4 weeks passes to a yellow syrup. If the β -acid be protected by brown glass, the softening does not occur until 3 months have elapsed.⁷² It must be noted that the β -glyceride absorbs oxygen very strongly in comparison with the β -acid. The α -acid can be transformed into the elaidin modification, either by the action of nitrous acid or by iodine and sulphur.⁷³ The transformation of the α -acid in alcoholic solution into the β -acid is comparatively slow, slower than the corresponding change of the glyceride, but it is quicker than in the case of the potassium α -salt. The evidence for the formation of the β -acid during oxidation of the α -acid is indefinite and is improbable in spite of Marcusson's opinion.⁷⁴ Maquenne⁷⁵ holds the view that the extreme readiness with which elæostearic acid undergoes oxidation has led to errors regarding its formula, which he maintains is $C_{18}H_{30}O_2$. J. Böeseken and H. J. Ravenswaay^{75A} consider that the elæostearic acids are stereoisomeric acids because of the molecular reactivity of the oil and acids. On the analogy of oleic and elaidic acids the α - and β -acids may exist in the following three isomeric forms:—



Bi-cis Form.



Cis-trans Form.



Bi-trans Form.

The bi-cis form must be ascribed to the α -acid, and the cis-trans form to the β -acid.

The methyl and ethyl esters of the α - and β -acids have been examined by Morrell,⁷⁶ who has shown that on distillation *in vacuo* the α -variety is transformed into the β -variety (b. p. $232^{\circ}/14$ mm. n_D^{15} 1.496), yielding the β -acid; moreover, the cerium α -elæostearate is completely soluble in ether, whilst the β -salt is insoluble.⁷⁷ The absorption of oxygen by the esters has been referred to previously. Ethyl β -elæostearate absorbs 11.1 per cent. of oxygen ($O_2 = 10.9$) and remains fluid. In the study of the oxidation of the cerous salts of the α -acid it has been shown that the absorption of dry oxygen, at the ordinary temperature, occurs in two stages, accompanied by a change of the metal from the cerous to the ceric condition. After 6 days' exposure, 9.8 per cent. of oxygen was absorbed, corresponding to the addition of one molecule of oxygen

at an ethenoid linkage, and only after the long exposure of 65 days and even 10 months, did the oxygen absorption correspond to that required for 4 atoms of oxygen per molecule of the acid. The oxidised ceric salt, containing 2 atoms of absorbed oxygen, gave on transformation into the acid a soluble and an insoluble part in light petroleum, the latter showing a strong peroxide reaction and corresponding, on complete analysis, to $C_{18}H_{32}O_4$ (I. V., 79). The peroxide acid slowly polymerised *in vacuo* and hardened to a varnish-like substance. After 14 days *in vacuo* the molecular weight, in glacial acetic acid, was 484—518 and it rose in 2 months to 654—691 ($C_{18}H_{32}O_4$ requires 312).

Lead α -elæostearate differs from the corresponding cerous salt and from lead linolate in being sparingly soluble in ether and much less soluble in varnish solvents than lead linolenate; the lead β -elæostearate is likewise sparingly soluble. The potassium and ammonium salts of both α - and β -elæostearate are crystalline substances sparingly soluble in water and lacking the emulsifying properties of the potassium salts of the series of higher fatty acids. The barium, calcium and silver salts of the β -acid are prepared by the usual precipitation method.

The preparation of metallic tungates is of importance. A tungate drier containing lead and manganese may be made by incorporating the metallic oxides with oil and adding previously made resinsates of lead and manganese. Such a metallic drier is soluble in a drying oil (especially a fish oil) at temperatures above 100° . For details as to the preparation and properties of a number of tungates, calcium, lead and manganese, precipitated and fused, reference may be made to Circular 120, *Paint and Varnish Manufacturers' Association, U.S.A.*⁷⁸

Other $C_{18}H_{32}O_2$ Acids.—In addition to tariric acid, ricinoleic acid ($C_{18}H_{34}O_3$) and ricinelaidic acid are transformed by abstraction of the elements of water into $C_{18}H_{32}O_2$ acids, one of which is crystalline, m. p. 53 — 54° , but is not identical with the corresponding acid obtained from ricinoleic nor with linolic acid. Ricinoleic acid, $C_{18}H_{34}O_3$, is the acidic constituent of the principal glyceride of castor oil. It has the ethenoid bond as in oleic acid, 9 and 10, and the hydroxyl group is attached to the number 12 carbon atom:—*



Reference has already been made to chaulmoogric acid, $C_{18}H_{32}O_2$, m. p. 36 — 38° , and hydnocarpic acid, $C_{16}H_{28}O_2$, m. p. 59 — 60° , obtained from chaulmoogric and hydnocarpic oils respectively.

* It is a *trans*-compound and is optically active; nitrous fumes convert it into the stereoisomeric ricinelaidic acid.

They are cyclic compounds containing only one pair of doubly-linked carbon atoms. They have no interest for the student of drying oils, as they have only therapeutic value.

Linolenic Acid Series, $C_nH_{2n-6}O_2$, $n = 18$.

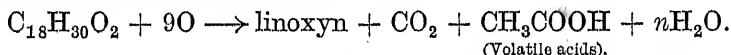
Linolenic Acid, $C_{18}H_{30}O_2$.—This acid possesses three unsaturated ethenoid linkages and offers opportunity for greater isomerism and confusion as to constitutional formulæ. As will be shown later, it is a component of many drying and semi-drying oils. It was first prepared by Hazura ⁷⁹ from its crystalline hexabromide (m. p. 177°) obtained from linseed oil acids. By reduction of the hexabromide with zinc and hydrochloric acid, Hehner and Mitchell ⁸⁰ obtained a nearly colourless oil (sp. g. 0.9228, 15.5°). It may also be prepared by boiling the hexabromide with zinc and alcohol, or by reduction of the ethyl ester of hexabromolinolenic acid and saponification of the resulting ethyl ester. The acid boils at 157—158° (0.001 mm.) without decomposition (Bedford), or at 230—232° (17 mm.).⁸¹ It is a colourless liquid, soluble in 10 parts of light petroleum. It absorbs oxygen readily and manifests a tendency to polymerisation, although definite proof of the latter is not forthcoming. The methyl and ethyl esters boil at 207° (14 mm.) and 132° (0.001 mm.) respectively. The melting point of linolenic acid hexabromide is 177—182° (185°, Coffey), and the melting point of its ethyl ester is 151°. Iodine and bromine trichlorides react to give trichloro-, tri-iodo-, $C_{18}H_{30}O_2I_3Cl_3$, and tribromo-tri-iodo-stearic acids, $C_{18}H_{30}O_2I_3Br_3$ respectively (m. p. 146° and m. p. 124—126°). Combination with hydrogen may be brought about by a nickel catalyst to give a quantitative yield of stearic acid (Erdmann and Bedford). A. Grün and W. Halden ⁸² give, as the hydrogenation value of unsaturated acids, the weight of hydrogen taken up by 10,000 parts of the substance which is theoretically equal to $2.016 \times n \times 10,000/M$, where n = number of double linkages and M = mol. wt. In the case of triple linkages the theoretical hydrogenation value is twice the above figure. The reduction may be carried out in a paraffin oil solution at 120—140°, using palladium-charcoal as catalyst. The hydrogen absorption is measured in a gas burette.

Erdmann, Bedford and Raspe (*loc. cit.*) state that two tri-ozonides are obtainable from linolenic acid, prepared by the reduction of the crystalline hexabromide, which are differentiated by their velocity of decomposition with water. The ozonides, on decomposition with water, give propionic aldehyde, malonic acid and the aldehydes of malonic and azelaic acids. It is on these

decomposition products that the constitutional formula of linolenic acid is based.⁸³ By oxidation with potassium permanganate Hazura obtained two hexahydroxystearic acids, $C_{18}H_{30}O_2(OH)_6$, linusic, m. p. 203—205°, and isolinusic, m. p. 173—175°, which fact does not support the existence of α - and β -acids, because either form of the so-called α - and β -linolenic acids yields linusic and isolinusic acids on oxidation (Rollett). It must be admitted that the Hazura method of oxidation is not satisfactory for quantitative work.⁸⁴

As to the existence of α - and β -linolenic acids in linseed or in perilla oil, the evidence is inconclusive, but there is a strong tendency on the part of investigators to accept their presence. The physical properties of the two acids are not sufficiently differentiated, as in the case of oleic and elaidic acids. Controversy between Erdmann, Bedford and Rollett is due to the fact that linolenic acid, from linseed oil, yields only 25 per cent. of hexabromo-acid on rebromination, and 77 per cent. of a tetrabromide of β -linolenic acid. Rollett maintains that the tetrabromide of β -linolenic acid is unsaturated and yields a hexabromide on further treatment with bromine. On bromination of linolenic acid, four bromo-addition products could be obtained (each of which could be resolved into two optically active isomerides), and if only one were crystalline then the 25 per cent. yield would be accounted for. The difficulty lies in the possibility of stereoisomeric changes during the absorption of the bromine, the reduction of the bromo-acid and subsequent bromination. The hexabromo-acid is insoluble in ether and chloroform, but soluble in alcohol, and melts at 180—181° (Coffey 185°) (*vide* analysis of drying oils). Attempts to fractionate the bromo-acid have been unsuccessful. Heiduschka and Lüft⁸⁵ state that they have obtained from *Oenothera biennis* (evening primrose) (the seeds of which contain 17 per cent. of a golden-yellow drying oil, similar to poppy-seed oil in taste and smell) an ether insoluble hexabromo- γ -linolenic acid, m. p. 195—196°. The oil is said to contain 2.5 per cent. of γ -linolenic, α -linolic 30.2 per cent., β -linolic 38.1 per cent. and oleic acids 29.2 per cent. The corresponding γ -hexahydroxystearic acid melts at 245° with decomposition. K. H. Bauer⁸⁶ obtained only linusic acid from the oxidation of the soluble brominated linolenic acids of perilla oil, but it is not safe to assume that the oxidation of β -linolenic acid yields only linusic acid. It would appear that three linolenic acids have been identified, one of which occurs in linseed oil, yielding a crystalline hexabromide, m. p. 180—185°; the second is formed by debromination and bromination of the first, and yields a liquid hexabromide, and the third is

indicated by the work of Heiduschka (*vide* Eibner, p. 48). Coffey, in an investigation on the oxidation of linolenic and linolic acids, showed that linolenic acid absorbed nine atoms of oxygen to give a peroxide linoxyn and volatile products consisting of carbon dioxide and acids (acetic acid). In the case of linolic acid there are no volatile products under the same conditions, and the oxygen absorption corresponds to the formation of a normal peroxide. It must be pointed out that peroxides and their aldehyde-decomposition products are prone to condensation, but the subsequent changes will be referred to in the chapter on the oxidation of drying oils. It will be sufficient to state here that the scheme for the oxidation of linolenic acid is, according to Coffey:—



The basic zinc salt, $[\text{C}_{18}\text{H}_{29}\text{O}_2]_2\text{Zn} + \frac{1}{2}\text{ZnO}$ (m. p. 72–73°), used by Erdmann⁸⁷ for the preparation of linolenic acid from linseed oil acids by fractional crystallisation from alcohol, has been found by Coffey⁸⁸ to be unsatisfactory, as it does not effect separation from linolic acid.

The lead and barium salts of linolenic acid are easily soluble in ether. The special drying properties of the metallic salts will be discussed in Chapter III. Like linolic acid, no isomeride of linolenic acid is obtained on treatment with nitrous acid.

A. Eibner⁸⁹ maintains that the yellowing of linseed oil films is due to the presence of free linolenic acid (produced by aqueous hydrolysis) or of its peroxide. It is noticeable that the yellowing effect is not apparent when poppy or nut oil films are subjected to the same conditions.

Acids from Marine Oils

Clupanodonic Acid, $\text{C}_{22}\text{H}_{34}\text{O}_2$.—Reference has been made to the unsaponifiable components of certain fish oils, especially dog-fish and shark-liver oils, whereas the saponifiable components contain a number of highly unsaturated fatty acid glycerides of $\text{C}_n\text{H}_{(2n-8)}\text{O}_2$ and $\text{C}_n\text{H}_{2n-10}\text{O}_2$ with $\text{C}_{14}\text{C}_{16}\text{C}_{18}\text{C}_{20}\text{C}_{22}$ carbon atoms.

From Japanese sardine oil, Tsujimoto⁹⁰ has obtained clupanodonic acid, $\text{C}_{22}\text{H}_{34}\text{O}_2$; with a decabromide, $\text{C}_{22}\text{H}_{34}\text{O}_2\text{Br}_{10}$, and not $\text{C}_{18}\text{H}_{28}\text{O}_2$ with an octobromide.

By brominating the mixed fatty acids of fish-liver and blubber oils in glacial acetic acid, and washing the precipitate with ether until the washings leave no residue, octobromides or decabromides ($\text{C}_{18}\text{H}_{28}\text{O}_2\text{Br}_8$ or $\text{C}_{22}\text{H}_{34}\text{O}_2\text{Br}_{10}$) are obtained. The octobromides

or decabromides blacken at 200° and on further heating decompose without melting. M. Tsujimoto and K. Kimara have investigated the acids in Japanese sardine oil,⁹¹ taking advantage of the solubility of the lithium salts of highly unsaturated acids in 95 per cent. acetone, whereas saturated and less unsaturated acids give

Oxidation of Clupanodonic, Linolenic, Linolic and Oleic Acids.

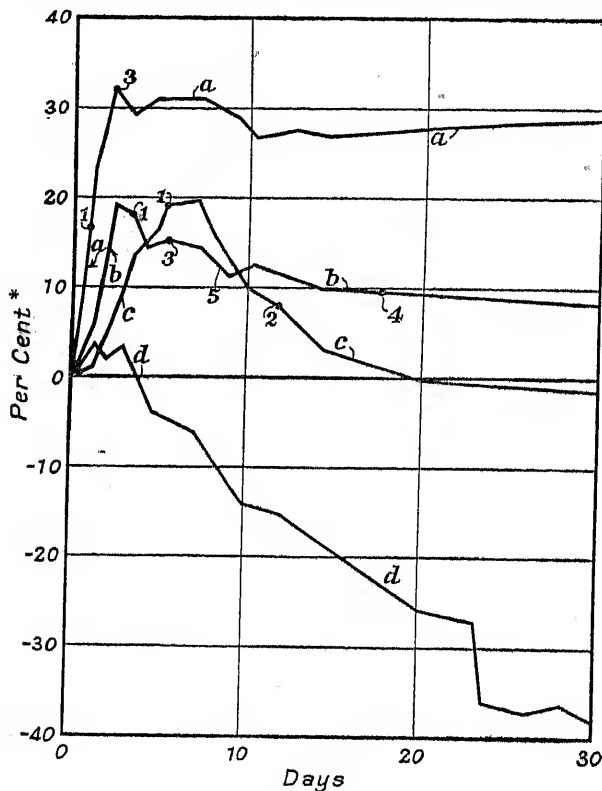


FIG. 2.

- | | |
|------------------------|---------------------|
| a = clupanodonic acid. | 1 = dragging. |
| b = linolenic acid. | 2 = tacky. |
| c = linolic acid. | 3 = free from tack. |
| d = oleic acid. | 4 = sweating up. |
| 5 = yellowing of film. | |

insoluble lithium salts. The method is not applicable to the fatty acids from sperm oil, as the lithium salts of phytsetoleic, $C_{16}H_{30}O_2$, and tetradecylenic ($C_{14}H_{26}O_2$) acids appear to be soluble in 95 per cent. acetone. Fractional distillation of the methyl esters allows of the separation of clupanodonic acid (sp. g. 0.9385/15°/4°, semi-solid at -78°, $n_D^{20} = 1.5020$; methyl ester, b. p. 222°/5 mm.). Among the other highly unsaturated acids of the oil, the acids

* Per cent. = percentage increase in weight of the oil film (Fig. 2).

$C_{18}H_{28}O_2$ and $C_{20}H_{32}O_2$ are probably present, but in much smaller quantities.⁹² J. B. Brown and G. D. Beal,⁹³ in an examination of menhaden oil, prepared methyl esters, b. p. 195—240°/15 mm., which, on bromination, contained 68.31 per cent. bromine. On reduction of the polybromides by zinc and methyl alcohol, esters were obtained which on fractionation gave practically pure methyl clupanodionate (b. p. 213—218°/15 mm., M.W. = 280.8, I.V. = 348.8, $n_D = 1.486$, Br = 68.62 per cent.). The corresponding bromide, methyloctobromostearate, melts at 240°. In addition to clupanodonic acid ($C_{18}H_{28}O_2$, which cannot be the same acid as that obtained by Tsujimoto) there are present hexadecatrienoic, $C_{16}H_{26}O_2$,* linolenic, arachidonic, $C_{20}H_{32}O_2$ [4], eicosapentenoic acid, $C_{20}H_{30}O_2$ [5], docosapentenoic, $C_{22}H_{34}O_2$ [5], and docosahexenoic $C_{22}H_{32}O_2$ [6] acids, as well as myristic and palmitic acids. The figures in brackets indicate the number of double bonds presumed to be present in the molecule of the acids. It is recorded that, in the process of bromination and debromination, structural changes occur which have been noticed under linolenic acids, and may be due to migration of linkages, ring formation or elaidin changes.

A. Eibner and E. Semmelbauer⁹⁴ have given an interesting summary of the investigation of fish oils. In 1854 Hofstadter⁹⁵ discovered in sperm oil an unsaturated, physetoleic acid, $C_{16}H_{30}O_2$. Bull⁹⁶ obtained from herring and cod-liver oils acids, $C_{20}H_{32}O_2$ and $C_{24}H_{38}O_2$. In whale and herring oils he found gadolenic acid, $C_{20}H_{32}O_2$, m. p. 24.5°. Eibner, from an examination of sardine oil (Japan), isolated a clupanodonic acid, $C_{22}H_{34}O_2$, yielding a decabromide, but with an iodine value of only 359 (calc. 384). The decabromide of the acid is with difficulty debrominated, but eventually yields on rebromination quantitatively the original decabromide, showing no evidence of isomerism during the change (cf. linolenic acid). Clupanodonic acid in thin film dries hard in 2 days, and in 6 days the film yellows (cf. linolenic acid). There is no loss of weight on exposure, as in the case of other drying oils (cf. Fig. 2, p. 42). The film dries glass hard, carbonises at 140°, has an iodine value 0, but it is more readily attacked by water than linolenic acid. Eibner draws attention to the high degree of its unsaturated character and to the properties required for a good paint oil.

It is evident that some new reaction or new reagent is required to effect the separation of the unsaturated acids of drying oils. In view of the complexity of the mixture, it would be hazardous to

* Hexadecatrenoic Acid [3] = Palmitolic Acid : Clupanodonic Acid [4] = Octadecatrenoic Acid.

assign structural formulæ to what are evidently unsaturated open-chain acids. No details have been published as to the special properties of their metallic salts, and the high melting point of the octobromides and dekabromides and their insolubility in ether seem to be their most characteristic properties.

Armstrong and Hilditch⁹⁷ have identified in whale oil from South Georgia glycerides of the following acids:—

Myristoleic acid (about 1.4 per cent. of the whale oil): $\Delta^{9:10}$ -tetradecenoic acid,



Palmitoleic acid (about 15 per cent. of the whale oil): $\Delta^{9:10}$ -hexadecenoic acid,



Oleic acids (about 35 per cent. of the whale oil): about 95 per cent. $\Delta^{9:10}$ -octadecenoic acid,



not more than 5 per cent. of an isomeric acid $\Delta^{11:12}$ -octadecenoic acid.

Polyethylenic acids (C_{20}) containing no double bond nearer the carboxylic group than $\Delta^{9:10}$ -position.

Polyethylenic acids (C_{22}) containing the double bonds further along the chain of carbon atoms than $\Delta^{9:10}$ -position.

Linseed Oil Acids.—During the Great War the demand for glycerine, together with the general shortage of fatty oils, brought forward the acids from linseed oil as a substitute for the glycerides in paint and varnish manufacture. Without going into a description of the attempts made to utilise the oil acids, it may be stated that the results were generally unsatisfactory. It is an interesting confirmation of the part played by the glyceryl group in the drying of linseed oil, although comparison of the true oxygen absorption curves of linseed oil and its fatty acids shows 28.7 per cent. for linseed oil and 30.1 per cent. for the fatty acids, whilst in the latter case the period of induction is shorter. Another difficulty is the presence of solid saturated acids, which have to be removed before the fluid portion can be used as a paint or varnish medium. The oil-acids are better solvents than the glycerides. Copals are easily soluble even when unsweated, but the solution gives a separation of the copal resin when thinned with turpentine. After the gum has been run in the oil-acids in the ordinary manner, the mixing will stand thinning with turpentine or petroleum spirit. The acids may be used as a solvent for rubber. For the preparation of metallic linoleates driers the linseed oil acids are quite suitable.

The solubility in alcohol enables the introduction of drying oil material into spirit varnishes, but it must be remembered that the oxidised film of the acids has not the durability of the ordinary linoxyn film (Morrell, "Varnishes and their Components," p. 91).

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CHAPTER II

THE COMPOSITION OF DRYING OILS

THE number of vegetable drying oils is large, but few have any industrial value. There are several factors which determine the demand for any drying oil: (a) the supply of the oil seeds from home or foreign cultivation, (b) adaptability of the seed to the ordinary conditions of crushing, (c) the utilisation of the press meal after the extraction of the oil.

It is advisable that all the products of the crushing process shall have a market value and, as far as possible, every part of the seed-producing plant. If these factors are considered, the number of vegetable drying oils in use is restricted. The following list shows the more important industrial drying oils: linseed oil (from many localities), tung oil (from species of *Aleurites*, some of which yield candle-nut oil and lumbang oils), perilla oil, walnut oil, poppy-seed oil, niger oil, sunflower oil, hemp-seed oil, chia oil and oiticica oil; the two last are in small demand and the latter fails to comply with condition (b), i.e., adaptability of the seed to crushing conditions. The less active drying oils are soya-bean oil, safflower oil and Para rubber-seed oil. Lewkowitsch lists 44 well-known drying oils and 17 lesser known. Castor oil is not included among drying oils, and its composition is approximately 80 per cent. ricinoleic acid, 9 per cent. oleic acid, 3 per cent. linolic acid and 10 per cent. saturated acids as mixed glycerides (Eibner).

The marine oils are represented by menhaden, sardine and herring oils. Among the large number of oils, all containing different proportions of a very limited number of component glycerides, the influence of factors, many unknown, on their properties is very striking.

The distribution and sources of linseed oil will be dealt with in the chapter on the extraction and refining of oils. Only the composition of the important drying oils will be considered.

Linseed Oil.—Genuine linseed oil contains essentially mixed glycerides of linolenic, linolic and oleic acids, together with glycerides of saturated acids, palmitic, stearic and possibly myristic and arachidic. The amounts of the less unsaturated glycerides vary with the maturity of the seed (cf. p. 19). Although the amount of the saturated glycerides is small, their presence is of importance, because of the sparing solubility of their lead salts in oil and varnish thinners. The composition of linseed oil, especially in view of changes taking place in the seed (p. 19), has been a matter of uncertainty for some time, and Eibner and Schmidinger are the

first to publish the results of a complete analysis. The following authors have also put forward conclusions as to the composition of the oil: Fahrion,¹ Friend,² Coffey.³

	Fahrion (1910).		Friend (1917).				Coffey (1923).		Eibner and Schmidinger (1923).	
	%.	Calc. I.V.	%.	Calc. I.V.	%.	Calc. I.V.	%.	I.V.	%.	I.V. oil.
Unsaponifiable matter.	0.6	—	—	—	—	—	—	—	1.0	—
Saturated organic acids	9.3	—	10	—	10	—	8.1	—	8.2	—
Oleic acid ...	17.5	15.8	5	4.5	5	4.5	5.0	4.5	4.5	—
Linolic acid	30.0	54.4	59.1	107.2	48.3	87.9	48.5	86.1	α 17.0 β 41.8	—
Linolenic acid	38.0	104.0	21.3	58.3	32.1	87.6	34.1	93.5	α 20.1 β 2.7	—
Glyceryl radicle ...	4.6	—	4.6	—	4.6	—	4.3	—	4.1	—
Oxy-acids ...	—	—	—	—	—	—	—	—	0.5	—
	100.0	174.2	100.0	170.0	100.0	180.0	100.0	184.1	99.9	173.3 ↓ 173.8

The above table summarises the knowledge of the composition of linseed oil up to date. The composition as given by Friend rests on calculation from the iodine values of the components, together with the yields of hexabromolinolenic acid. In addition, Coffey estimates the amount of α -linolenic acid present from the amount of carbon dioxide and volatile acids obtained in the oxidation of the linseed oil acids, as indicated on p. 41. The iodine value of the mixed acids, linolenic, linolic and oleic, being known (the oxygen absorption of linolenic and linolic having been determined directly), the amount of oleic acid present is obtained. The figures given by A. Eibner and K. Schmidinger result from a complete chemical analysis of the oil, including a determination of the solid fatty acids. The oil examined was of Dutch origin and had iodine value 173.5, acid value 2.3; it contained α -linolenic acid, 20.1 per cent., β - or iso-linolenic acid, 2.7 per cent.; α -linolic acid, 17.0 per cent., etc. The content of α -linolenic acid and α -linolic acid was determined from the hexabromide value and the bromine content of the mixture of solid hexa- and tetra-bromides, using Hehner and Mitchell's formula.⁴ The content of isolinolenic acid was calculated

from the amount of oily bromo-acid which was present in the filtrate from the hexabromide test, and which yielded linolenic acid on debromination. The ratio of β -linolic acid to oleic acid was obtained from the bromine content of the filtrate from the hexabromide determination, allowance being made for the bromide of isolinolenic acid also present. The sum of β -linolic acid and oleic acid is calculated from the iodine value of the oil, the values already found for the other unsaturated acids being inserted. The figures for α -linolenic and α -linolic acids are considered quite trustworthy, but account for only 54 per cent. of the composition of the oil, whereas those for isolinolenic, β -linolic and oleic acids are only approximate.

An attempt was made to identify the mixed glycerides in the oil and the results have been already referred to on p. 21. Part of the oleic acid, separated as di-elaïdopalmitin, must be present as a mixed glyceride, a form in which it is less harmful to the oxidised film than as triolein. The second mixed glyceride, isolated to the extent of 25 per cent. of the oil, was identified as di- α -linolenic- α -linolic glyceride. The forms in which the rest of the acids and the remainder of the oleic acid are combined remain unknown. The nature of the mixed glycerides has an important bearing on the technical properties of the oil, *e.g.*, the presence of triolein would transform a drying oil into what is practically a semi-drying oil in that the oxidised film would never harden. The following table shows the characteristics of some varieties of linseed oil :—

	S. G. (15°).	$n_{D_{20}}$.	Sap. val.	Acid val.	Iodine val.	Oxidised acids.	Unsep. matter.	% Oil in seeds.
Baltic	0.932—0.941	1.4830	189—192	1.28—1.56	190—204	0.7	1.0	32—38
	0.932	—	189.5	1.85	191.5	0.7—1.0	1.1	39 (stepped seed)
Calcutta oil...	0.9282	1.4822	189	0.8	170—190	0.65	0.7	37—41
	0.9289	—	192	4.9	177.5—183	—	—	37—43
Dutch	—	—	—	—	191—208	—	—	35—55
Chinese linseed oil ...	0.935	—	—	1.37	{ 181.6 } { 194 }	—	—	—
American ...	0.932; 0.936	{ 1.4805 } { 1.4790 }	195	1.6	{ 189.1 } { 178—194.6 }	—	1.5	36—38
Canadian....	0.9340	—	209	1.6	186.4	—	—	—
Morocco	—	—	—	—	189—193	—	—	36—40
(Mazagan).	—	—	—	—	—	—	—	—
Argentine ...	0.9310	—	—	2.1	177:175—189	—	—	35—38.5
English	0.939:0.929	—	198.9	2.5	196.5—200.4	—	—	—

The figures in the above table show comparatively small differences in linseed oil from various sources. Baltic oil is still largely favoured because of its superior drying properties and more rapid thickening when heated; there are also advantages for its use in some cases where the colour of a mixing has to be considered. In the series, superior drying and thickening power would be indicated

by a higher iodine value, but many of the special properties are difficult to forecast from the data given. Nevertheless the figures are of value because when once the choice has been made of a certain variety, the characteristics given serve for purposes of identification.

H. Wolff ⁵ on theoretical grounds has deduced a formula connecting the value of the refractive index with density, acid value and iodine value, which he states gives results within 0.0003 unit of those found experimentally for fatty open-chain acids.

$$n_D = 1 + d(0.557 - 0.00022s + 0.000035I)$$

[n_D =refractive index; d =density; s =acid value; I =iodine value.]

The oxidation and polymerisation of linseed oil will be discussed in detail in Chapters III and VI. For details of the preparation of precipitated and fused linoleates of cobalt, manganese, lead and zinc, reference may be made to H. A. Gardner and R. E. Coleman, *Circ. 120, Paint Manuf. Assoc., U.S.A.*

Specifications for raw and refined oil put forward by the U.S.A. Inter-departmental Committee on Paint Specifications, 1919, may be briefly summarised as follows:—

	Raw linseed oil.		Refined linseed oil.	
	Max.	Min.	Max.	Min.
Loss on heating @ 105—110°...	0.2	—	0.2	—
Refractive index	—	—	—	—
Mucilage by volume	2.0	—	—	0.2
Sp. g. @ 15.5°	0.936	0.932	0.936	0.932
Sap. value	195	189	195	187
Acid value	6.0	—	9.0	—
Unsapon. matter %	1.5	—	1.5	—
Iodine value (Hanus)	—	170	—	170
Colour not darker than 1 gr. $K_2Cr_2O_7$ freshly dissolved in 100 grs. H_2SO_4 , s. g. = 1.84.			Colour not darker than 0.1 gr. $K_2Cr_2O_7$, similarly dissolved.	

A British Engineering Standards Specification for linseed oil will be published shortly.

China Wood Oil (Tung Oil).—This oil contains glycerides of α - and β -elæostearic acids, together with small quantities of olein and glycerides of saturated acids. It is the product of oil seeds of certain species of *Aleurites*, whose occurrence and distribution will be given in a later chapter (Chap. IV). The following table shows the most important characteristics of the oils extracted from Chinese,

Japanese and East Indian varieties of *Aleurites*. China wood oil is obtained from *A. Fordii* or tung-yu shu, tung oil tree, and *Montana*, mu-yu shu, wood oil tree. The Japanese variety is obtained from the seed of *A. cordata*, or *abura kiri*, whilst *A. triloba* yields candle-nut oil and *A. trisperma* (banucalag nuts) gives lumbang oil.⁶

The oils differ markedly in properties, not only in the drying power of the film, but in the rate of gelatinisation.⁷

	S. G. 15°.	n_D 25°.	Reichert-Meißl value.	Acid val.	Sap. val.	Iod. val. (Wijs).	Unsap. matter.	Gelatin. (Browne's) test.	Drying time (min.) 95°.	Oil content %.	
										Seeds.	Endosperm.
<i>A. Fordii</i> (China)	0.9488	1.5210	0.89	1.52	196.76	157.17	0.59	10 min.	55	44	66.3
<i>A. cordata</i> (Japan).	0.934	1.5005	1.10	0.47	194.8	150.9	0.41	viscous	65	37.8	59
	0.9342	1.4981		3.9	185—197	154.2* (Hanusa)					
<i>A. montana</i> (Kangtong, India).	0.9372	1.5147	0.35	0.59	194.3	154.85	—	16 secs. (J., 1920, 604A).	60	37.4	59.8
	0.9467	1.494 (15°)		3—4	205	141.4					
<i>A. moluccana</i> (Bakoly).	0.9207	1.4785	0.7	0.8	195	146.3	0.07	viscous	270	23.6	70.6
	0.9206 (81°)	1.475				154 (Hanusa)					
<i>A. triloba</i> (candle-nut oil, Ceylon).	0.9222	1.497 (25°)	—	3.3	175	140	—	viscous	—	—	—
	0.927	—	—	0.7	216.4	146.5					
<i>A. trisperma</i> (lumbang).	0.980	—	—	2.2	161	187	—	viscous	—	—	—
						162 (Hanusa)					
						166 (Hanusa)					

* Wijs' method gives 2 units lower than the Hübl method.*

The blending of the oils from different varieties of *Aleurites* is common and leads to complications which may be illustrated as follows:—

	I. V.	Colour.	S. G.	Gelatinisation.
<i>A. Fordii</i>	173	Amber.	0.942	Complete on heating. Very slight gelatinisation on heating.
<i>A. triloba</i>	140	Almost white.	0.925	

Like all other oils, China wood oil varies as regards its chemical and physical properties, but it may be said that the great variations of the source of production, as well as the natural conditions met with in the producing areas, have a greater effect than is probably the case with any other known variety of a common drying oil. The Hankow and Japanese products are quite distinct from what is known as Canton wood oil. The last-named passes chiefly through Hongkong mercantile houses, many of which have suffered heavy financial losses, owing to the oil containing adulterants some-

times amounting to 10 per cent. of the oil. It is said that more tests and analyses have been made on China wood oil than on any other drying oil except linseed oil. European supervision of the crushing of the seed is almost impossible, especially in the case of the variety from southern China. Adulteration with native bean oil, especially soya oil, is a common practice. Hankow is the chief port of export and 80 per cent. of the oil is shipped from there. From analyses of seventeen samples of genuine Hankow oil Chapman⁹ proposed the following standards, which may be compared with the recommendations of the Amer. Soc. Test. Matls., U.S.A.¹⁰

Chapman.

	S. G. (15°).	I. V. (Wijs).	A. V.	S. V.	$n_D^{20^\circ}$.	Vis- cosity.
Maximum	0.9440	176.2	12	196.6	1.5207	2178
Minimum	0.9406	166.4	—	192	1.5170	1636
Average	0.9425	170.6	7.6	194.2	1.5179	1850

Amer. Soc. Test. Matls.

	S. G. (15°).	A. V.	S. V.	Unsap M. %.	$n_D^{25^\circ}$.	I. V.
Maximum	0.943	8.0	195	0.75	1.520	—
Minimum	0.940	—	190	—	1.515	163

Heating test, minutes : maximum 12.

It appears to be practically impossible to obtain a really authentic sample of strictly pure wood oil. The refractometer figures are the most reliable characteristics in deciding on adulteration.¹¹ The variation in the refractive index with temperature of China wood oil is 0.0004 per 1°.¹² The term "pale," as applied to wood oil, has no special significance. For details as to the correct mode of sampling wood oil, reference may be made to a communication by C. V. Bacon.¹³ The oil from *A. Fordii* is composed essentially of glycerides of α -elæostearic acid and traces of the β -modification. Olein is present to the amount of 10—15 per cent. (Fahrion states that 2—3 per cent. solid saturated acids are present, and M. Nonaka has shown the presence of 2.5 per cent. stearic acid).¹⁴ *A. montana* from India is stated by R. N. Parker and collaborators (*loc. cit.*) to contain the glyceride of β -elæostearic acid without the α -isomeride,

together with oleic and linolic acids, but no linolenic acid. The oil from *A. triloba* (lumbang oil) contains linolenic acid 6.5 per cent., linolic acid 33.5 per cent., oleic acid 57 per cent. and oxidised acids 2.8 per cent., but elæostearic is absent (cf. composition of linseed oil).¹⁵ *A. moluccana* remains fluid at 315° and, if held at that temperature, begins to distil regularly, gelatinising when one-third has been expelled. The oil from *A. trisperma* fails likewise to gelatinise readily. The literature on tung oil is very extensive.¹⁶ Tung oil has marked peculiarities, differing from linseed oil in the following respects: specific gravity, iodine value, refractive index and its property of gelatinising on heating.

	S. G. (15°).	I. V. (Wijs).	S. V.	$n_D^{25^\circ}$.	Gelatinisa- tion (Browne's test).	A. V.
Max.	0.943	163 (Wijs)	195	1.520	12 min.	6-8
Min.	0.940-0.939	165 (Hüb.)	190	1.5165-1.515	—	(latest values)

It dries in about two-thirds of the time of linseed oil, giving a film which is white, dull, opaque, and crinkled. If the film be allowed to dry in a moisture-saturated atmosphere, the solidification is very much retarded, but it is clear and free from the wrinkles observed in the previous case. The typical matt effect is especially marked if the drying proceeds in a gas-laden or foul atmosphere. In the presence of metallic driers, the surface defects of the film are very much reduced. The surface puckers or webs and becomes matt, with a finely radiating crystalline appearance or uniform opacity like ground glass, whenever the conditions are unfavourable to uniform oxidation. If the drying be performed at temperatures above 80°, in a good draught, the film is transparent and smooth. The webbing and fine cracking are due to unequal volume changes in the film on surface drying. The matt surface has been considered by Marcusson¹⁷ to be due to the formation of crystals of β -elæostearin. This crystalline stereoisomer, a monomolecular glyceride of β -elæostearic acid, is rapidly oxidised to an amorphous, white peroxide.¹⁸ A microscopical examination of a matt film shows no evidence of crystalline formation. The formation of the isomeric acid requires light of appreciable actinic value, whilst "webbing" takes place readily in the absence of light, when the conditions of oxidation are unfavourable; moreover, a non-matt surface can be obtained from tung oil by allowing it to dry in a very thin film.

The opinion expressed by H. Wolff¹⁹ against the formation of the isomeric glyceride is probably correct.

The high dispersive power of the oil is one of its characteristic properties, the dispersive power $\frac{n_F - n_D}{n_D - 1}$ at 40° for typical vegetable oils being as follows: China wood oil, 0.0371; linseed oil, 0.0218; cotton-seed oil, 0.0195; castor oil, 0.0190, and coconut oil, 0.0167.

Fahrion's hypothesis, that the high viscosity of the oil and the resulting slow diffusion of the oxygen therein is responsible for unequal volume changes in the top skin and under layer, is generally accepted. It is evident that the first stage of the gelation is the production of a solidified (oxidised) oil phase, dispersed in unoxidised oil. The uniformity of the formation of the oxidised gel, allowing of diffusion of the continuous phase of the unoxidised oil to the surface, will play an important part in the production of a clear film. The linoxyn film is not impermeable to moisture and gases. The rancidity of the dried wood oil film is very marked, and indicates decomposition of the oxidised oil around the ethenoid linkages remote from the carboxyl radicle.

Another peculiarity of tung oil is its rapid gelatinisation on heating.²⁰ When heated to 282° for 9 minutes (Browne's heat test) it sets to a hard transparent jelly. This property is used for the detection of impurities in the oil, and it is stated that the addition of 5 per cent. of another oil, *e.g.*, soya-bean oil, will retard the gelatinisation at the above temperature.²¹ The gelatinisation is due to polymerisation, which differs greatly in rate from that of linseed oil. It is stated by various observers that solvent extracted oil does not polymerise as easily as expressed oil, which is difficult to understand. The oxidation and gelatinisation of tung oil will be discussed in Chapters III and VI. Tung oil has the following uses in China: as a wood varnish, for the caulking of boats, as a component of lacquers, as a waterproofing agent for cloths, silk and leather, as a varnish for furniture and in the production of papier maché. The soot from burnt wood oil produces the best quality Chinese ink, and the oil has a limited use as an illuminant and as an emetic and purgative. In Europe and in America it is in demand, owing to the improved water resistance and durability which it confers on varnishes which contain it. The use of China wood oil has allowed the introduction of rosin in varnish manufacture, especially as calcium resinate or as the rosin glyceride ester, which can be used in place of the fossil resins of the so-called

copal varnishes. The phenomenon of chalking or spotting of varnish mixings in contact with water is much reduced if wood oil be present, but, as appears to be the case with the majority of resin oil mixings, improvement in the water-resisting properties is accompanied by the greater tendency to condense water on the surface. The film of China wood oil is an active polar surface, probably due to imprisonment of unoxidised wood oil in the surface film.

For details as to the preparation of precipitated and fused tungates of calcium, lead and manganese from China wood oil, reference may be made to *Circ. 120, Paint Manuf. Assoc., U.S.A.*, H. A. Gardner and R. E. Colman, "Notes and Suggestions on the Manufacture and Use of Metallic Soaps in Paint and Varnish Making."

Candle-nut Oil.—Candle-nut oil from *A. triloba*²² of Fiji, and Hawaii, West Indies and Brazil, may be used to replace linseed oil in the manufacture of paint and linoleum, but it is more suitable for soap manufacture. The characteristics of the oil are: S.G., 0.927 (15°); Sap. V. 175; I.V. 137, and free fatty acids (oleic acid), 0.7 per cent. The low iodine value indicates its inferiority compared with linseed oil, for drying. It would find a ready sale for the large quantities available if its transport to the consumer were facilitated. In Madagascar the oil expressed from the nuts is known as "bakoly" oil. In India it is called "kekuna" oil.

Lumbang Oils.—Lumbang oil is obtained from *A. moluccana* (lumbang bato nuts), and soft lumbang oil from *A. trisperma* (lumbang banucalag nuts).²³ The first-named *Aleurites* is the commoner source of the oil, the latter not being utilised, since it is said to cause skin eruptions on those handling the oil. Lumbang bato oil is stated to be as good as linseed oil, and either can be used as a substitute for the other.²³ It has been tested in zinc and iron oxide-paints, in varnishes, polishes, printing inks and rubber substitutes, in comparison with linseed oil. The manufacture of lumbang oil is carried on by Chinese workers in a very primitive manner. A supply of 230 metric tons per month for a factory could be maintained.

The oil is used locally for caulking boats, in the manufacture of soft soap and in paints. The shell of the nuts, amounting to 66 per cent. of the total weight, is hard and tough and extremely difficult to remove, the operation being performed by hand, either after sun-drying and boiling with water, or by heating over a fire and quenching in water.²⁵ There is a great demand for the oil in the United States. A. P. West and Z. Monte²⁶ give the following

description of the seeds of *A. moluccana*: 66 per cent. shell, 34 per cent. kernel, containing 50—60 per cent. of oil having S.G. 0.9206 ($31^{\circ}/4^{\circ}$); I.V. 140 (Hanus). The oil is stated to consist of 6.5 per cent. linolenic, 33.4 per cent. linolic, 56.9 per cent. oleic, and 2.8 per cent. glycerides of solid acids. It dries quickly, is not polymerised at 200° and is free from elæostearic acid. K. H. Bauer,²⁷ A. P. West and A. I. de Leon²⁸ have made a comparison of the blowing of lumbang and linseed oils at 75° . For the first 30 hours lumbang oil absorbs oxygen more rapidly than linseed oil, but after 40 hours the two oils have absorbed the same amount of oxygen. The characteristics of the two oils blown for the same period are nearly the same, although from the figures given above raw lumbang oil contains considerably more oleic acid than is found in linseed oil. In spite of the favourable comparison it is hardly likely to be a serious rival to linseed oil in Europe.

Perilla Oil.—Perilla oil is obtained from the seeds of *Perilla ocymoides* (*Nankinensis*), Asiatic mint, an annual plant growing in Manchuria, Japan and the East Indies. The seeds contain 38 per cent. of oil, and both oil and cake are edible like linseed. In Japan it is employed as an adulterant of lacquer, and the Japanese crop is estimated at 325,000 bushels per annum. The cultivation of the seed is being studied in N. India, the East African Protectorate, South Africa, Cyprus and Rhodesia,²⁹ also in America and in Canada. A certain amount of the oil is being used in England and America and in sufficient quantities to warrant the issue of a standard specification by the A.S.T.M. (Standard Specifications for perilla oil, raw or refined, D 125, 22T).

Perilla oil, raw or refined, should conform to the following requirements (A.S.T.M.) :—

	Maximum.	Minimum.
Foots, %.*	2.5	—
Loss on heating at $105-110^{\circ}$ %	0.2	—
S. G. at 15.5°	—	0.932
Acid number	5.0	—
Saponification number	—	190
Iodine number (Hanus)	—	191
Unsaponifiable matter, %	1.5	—

Colour not darker than a freshly prepared solution of $K_2Cr_2O_7$ in 100 c.c. H_2SO_4 (s. g. 1.84).
 (Hexabromide value of fatty acids (Steele and Washburn method): 148—150.)³⁰

* See chapter on Analyses of Drying Oils.

A comparison with linseed oil is given by Lanks,³¹ Bauer and by one of the authors :—

	S. G.	A. V.	I. V.	S. V.	Refractive index.
Perilla oil *	0.9343 (15°) 0.9280 (20°)	3.7—6.7	182.4—190.1 (Wijis) 196—206 (Hanus) 204 (Hanus)	188.5 190.6 187.4	1.4841 (20°) 1.4840 (25°) 1.4830 (20°)
Linseed oil	0.932—0.9360 0.933—0.9340	— —	180 174—184	— —	1.4790 1.4775

* Perilla oil showed no foots in the breaking test; the colour of the clarified oil was fair, whilst raw linseed showed 3.3 per cent. foots.

Considerable attention during the last few years has been paid to the investigation of this oil, both in China, Germany and America. C. T. Wang³² encourages the revival of the industry in Japan, and goes so far as to state that it is superior in drying properties to tung oil. J. A. Hongler³³ considers that the supply of the oil is insufficient to make it a substitute for linseed oil generally, but in specialities its merits will be recognised. Perilla oil produces a hard, lustrous, tough and waterproof film. In the raw state it is said to have a tendency to creep and form drops when spread on a surface, but this statement is not generally accepted by users of the oil. It is also stated that, when raw or improperly treated, it dries with a dull finish. The dried film is noticeably harder than that of linseed oil, but it discolours more rapidly with age. These defects can be overcome by heating to 293—315° for 1 hour or more if a heavier body be required. Its high iodine number, which averages 200, indicates that its oxygen absorption is greater than that of linseed oil. If raw linseed and perilla oil be tested, the latter shows a considerable advantage in time of drying, although the range of times varies from 24—40 hours,³⁴ but if both are given the same quantity of any good drier, the perilla will set and harden first. The rate of polymerisation or thickening on heating is much less than that of tung oil and greater than that of linseed oil, about 33 per cent. less time being required with perilla oil to reach a given consistency than with refined linseed oil. On blowing, the bleaching action is very great, bodying is also very rapid. The boiled perilla oils are remarkable for their extremely rapid drying and hard films. The films, however, discolour with age more strongly than those of boiled linseed oils. Perilla oil can be used with

advantage to dilute tung oil. In the kettle or with air the oil thickens very rapidly; the resulting product is a beautiful oil, light in colour, with more gloss than linseed oil. It will take more thinner without detriment to its durability, and it dries faster to a hard film and shows as good and perhaps better weathering qualities than linseed oil in varnish mixings. Undoubtedly varnish mixings containing it require much less manganese driers. In making enamels with perilla oil J. A. Hongler considers that a better product can be obtained by its use, because of the reduction in the amount of drier and resins. The films containing the oil do not "web" like the corresponding tung oil films. It can be easily bleached by fullers' earth when heated to 270° , and it does not darken afterwards. H. A. Gardner³⁵ reports favourably on the use of perilla oil in paints and in linoleum. Adequate polymerisation will much reduce the tendency of films to discolour. The authors consider that it is a valuable substitute for linseed oil, possessing in many ways superior properties; but its present high price, compared with that of linseed oil, will restrict its use except for special varnish mixings. K. H. Bauer and R. Hardegg, and K. H. Bauer³⁶ alone, have carefully investigated the composition of the oil. It contains 12 per cent. of saturated (palmitic) and 88 per cent. of unsaturated acids as determined by Pb salt-ether method. The investigation of the unsaturated acids on oxidation by potassium permanganate gave tetrahydroxystearic acid, m. p. $135-140^{\circ}$ (Nicolet and Cox), isolinusinic acid, m. p. $173-175^{\circ}$, and 25 per cent. linusinic acid, m. p. 201° , as well as a mixture of these acids. Oxidation of linolenic acid from perilla oil gave linusinic, isolinusinic acid and possibly other hexahydroxystearic acids. The unsaturated acids obtained by debrominating the bromides soluble in ether and glacial acetic acid gave on oxidation dihydroxystearic acid, corresponding to oleic acid. The hexabromostearic acid, m. p. 180° , from perilla oil [hexabromide number (Eibner) 50.8] was the same as from linseed oil.

Under the conditions of the investigation these authors show the presence of palmitic, oleic, linolic and linolenic acids, but they are unable to state definitely as to the existence of one special form of linolenic acid in the oil.

Soya-bean Oil.—Soya-bean oil³⁷ is obtained either by expression or solvent extraction from the seeds of *Soja hispida* or glycine soja, a leguminous plant grown extensively in Manchuria, Japan and China, thriving to the best advantage in a fairly fertile and moist loam. It was practically unknown in this country before the

Russo-Japanese War. Since that time the use of the oil and press-cake has spread greatly. Within recent years the plant has been introduced and cultivated in India, Ceylon, South Africa, Australia and South America. Soya seeds and the oil have been used in the East for centuries for edible purposes, and the seeds are a staple article of food in China. It is recorded that soya bean was cultivated in China for edible purposes in 3000 B.C. The soya plant grows to a height of 36—40 inches, branching into hairy stems, carrying about 40 pods per plant, each pod holding 2—5 seeds. The soya flowers are pale lilac in colour and are self-pollinating. The yield of soya bean per acre in Manchuria is 28 bushels, from a sowing of 20 lb. per acre. The climatic and soil conditions appear to influence seriously the oil content of the seed obtained. The yellow soya bean contains the highest oil and protein content and the black the lowest. The Hokkaido bean contains the highest protein and the least fibre content. Fellers³⁸ found the oil content of 26 varieties of seed to vary between 15 and 26 per cent. (a ton of beans will produce between 35 and 38 gallons of oil), the deciding factors in particular varieties being the length of the growing season, time of planting, time to reach maturity and the state of the seed when crushed. H. Low³⁹ gives an analysis of soya-bean oil as follows:—

S. G., 0.929; S.V., 190—201; A.V., 0.8—3.1; unsaponifiable matter, 1.16; I.V., 124.30, 133.8. Total fatty acids, 94.66 per cent. Reacting weight of fatty acids, 279.30.

The Department of Agriculture of the U.S.A. recognises 280 varieties of soya bean. The various types vary in colour between white, yellow and black, and in shape from spherical to elliptical. The composition of typical varieties of soya bean are given by Lewkowitsch (Vol. II, p. 115).

The soya bean industry of Japan is of enormous dimensions. It is estimated that there are over 10,000 soya-bean crushing establishments in the country. In 1911 Manchuria exported 1,500,000 tons of soya beans, 300,000 tons of which came to European countries, the remainder going to China and Japan. The current price (January 1924) of soya bean in England was £13 per ton. The imports of soya beans into the United Kingdom have increased from 59,357 tons in 1922 to 113,062 tons in 1923, and the imports of soya-bean oil from 20,357 tons in 1922 to 23,606 tons in 1923, of which 8097 tons were exported in 1922 and 7549 tons in 1923, together with exports of soya-bean cake of 4142 tons in 1922 and 13,442 tons in 1923. In the United States in 1920, 196 million

lb. of oil were imported, and in 1921 the imports had fallen to nearly 50 million lb., but the United States is now producing soya oil from home-grown beans. In six or seven months in 1920 more than 100,000 gallons of soya oil were produced. In those sections of the U.S.A. where the cotton fields are infested by the boll weevil, the growers may find it to their advantage to produce soya beans on a large scale.

The major portion of the soya-bean oil produced in Manchuria is still obtained by crude native methods. The beans are first dried and then bruised in a primitive machine driven by oxen. They are then allowed to stand in a tank of water for about 24 hours, well macerated with warm water and crushed so as to express the oil. The native oil press consists of a cumbersome wooden machine wedge—driven or rotated by oxen. The native presses are now being replaced by modern machinery, principally of Japanese manufacture.

The pressed cake is used extensively in Manchuria and Japan as a staple article of diet, and in 1923 250,000 tons of soya-bean cake were exported to Japan and China to be used for this purpose. In European countries the pressed cake is used as a valuable cattle food, the protein contents being greater than that in cotton-seed cake and only slightly inferior to that of linseed cake. In Denmark and Holland, soya cake is superior to cotton-seed cake as a cattle food, but in England decorticated cotton-seed cake commands a higher price than soya cake, because of its "scouring" action on the stock. It is used extensively in Japan and in China for fertilising mulberry trees and also for "forcing-beds" for sugar and rice nurseries. As a cattle food soya cake is readily digested and contains both the water-soluble and the fat-soluble vitamins. There are two types, soya cake and soya meal, the former being a product of pressing and the latter of solvent extraction. A description of the Anglo-American and the Cage systems for expression of the oil will be given in Chapter IV, whilst the solvent extraction process by the use of benzene, trichloroethylene and carbon bisulphide, to be described in that chapter is directly applicable to the treatment of the soya bean, as well as the processes of refining and bleaching. The prices of soya seed and soya-bean oil have fluctuated considerably during the last 10 years. In 1914 soya beans and soya-bean oil were quoted at £9 and £24 respectively; in 1920 the prices were £22 and £71 respectively; in 1923 £12 and £38; in January 1924 £13 and £43. High quality beans, free from fermentation products, yield an oil almost free from fatty acids, which can be used direct

for the majority of industrial processes. The crude or raw oil, after it has settled, finds application in the manufacture of soaps, paints, linoleum, and in foundries in the manufacture of "cores." Precautions have to be taken in transport to prevent rapid fermentation of the seed. Soya-bean oil used for edible purposes is refined by first eliminating any free fatty acids, and then deodorising and decolorising by treatment with fuller's earth, charcoal or by exposure to ultra-violet light. The presence of hulls in the crushed beans gives the oil a brown colour, and is very detrimental to the production of a high-grade oil. The oil finds application on the Continent as an ingredient of margarine manufacture, as a general edible oil and to a lesser degree as an illuminant. In Germany it is used for the preservation of fish, as a lard substitute, and is fast replacing cotton-seed oil for edible purposes. Reference to the nature of the oil of soya-bean miso by R. Kodama⁴⁰ will give some idea of the way in which soya beans and rice are worked up to make a staple native food in Japan. The soya bean contains 18 per cent. of oil, of which 10—13 per cent. can be extracted by the Anglo-American process; against this low yield must be set the fact that the harvest of the bean is large—20—30 bushels per acre—and the pressed cake is rich in protein. It is made into biscuits, vegetable cheese and a kind of pickle (soy). The emulsification of the oil, with gluten and casein-like bodies, is the basis of some patents for artificial milk.⁴¹ The emulsifying power seems superior to that of other drying oils.

The composition of soya-bean oil is 96 per cent. glyceryl esters, containing 15 per cent. saturated fatty acids (palmitic acid), 56 per cent. oleic acid, 20 per cent. linolic acid and 5 per cent. linolenic acid, with unsaponifiable matter containing stigmaterol and unsaturated oxygenated compounds.⁴² Keimatsu⁴³ states that the composition is: 12 per cent. stearic and palmitic esters, 50 per cent. linolic esters, 15 per cent. linolenic esters, 15 per cent. oleic esters and 0.2 per cent. phytosterol. W. B. Smith⁴⁴ gives the following composition: 9—10 per cent. stearic and palmitic esters, 55—57 per cent. linolic esters, 2—3 per cent. linolenic esters, 26—27 per cent. oleic esters. The low iodine value, 130, with an ether-insoluble bromide value of 7.8, indicates that its oxygen absorption will be low. The carbohydrates of the soya bean have been found to consist of non-reducing sugars and the cell membrane to consist of hemi-cellulose. W. F. Baughman and G. S. Jamieson⁴⁵ state that the approximate composition of the oil is as follows: saturated acids 11.9 per cent., consisting of palmitic 6.8 per cent., stearic 4.4 per

cent. and arachidic with lignoceric acids 0.7 per cent.; unsaturated acids 83.5 per cent., consisting of oleic acid 33.4 per cent., linolic 57.5 per cent., linolenic acids 2.3 per cent. and unsaponifiable matter 0.6 per cent. Matthes and Dahle⁴⁶ found palmitic acid, but no stearic acid, together with oleic 26—27 per cent., linolic 55 per cent., and linolenic acids 2 per cent. E. S. Wallis and G. H. Burrows⁴⁷ give the following figures: palmitic acid 6.8 per cent., stearic acid 4.4 per cent., arachidic acid 0.7 per cent., linolenic acid 2.3 per cent., linolic acid 51.8 per cent. and oleic acid 33.6 per cent.

The presence of cotton oil in soya oil can be established by means of Halphen's colour reaction, when the former is present to a greater extent than 5 per cent. A characteristic test for soya oil is treatment with uranium acetate in a chloroform solution of gum arabic, a yellow emulsion being produced; linseed oil gives a brown coloration. This test will show the presence of more than 5 per cent. of soya oil in earth-nut, cotton-seed, rape and coconut oil.⁴⁸ Utz⁴⁹ considers that this test needs further investigation in view of the introduction of the new African oils. A novel electric method for determining the purity of a specimen of soya oil has been proposed by Dall' Acqua.⁵⁰ The genuine oil, when subjected to the discharge of an electroscope of the Elster and Gester type, conveyed the discharge in less than a second, a rancid and long-exposed specimen taking 1.6 seconds. The lowest of the other vegetable oils was 15 seconds and varied up to 100 seconds. The following characteristics have been ascribed to the oil: S.G. (15°) 0.9225—0.9240; solidifying point, —8° to —15°; S.V. 188—192; I.V. 130—140; Hehner value, 96; acid value, 0.20—1.9; refractive index (20°) 1.475, (40°) 1.468; Maumené test, 88°. Characteristics of the fatty acids: solidifying point, 21.2°; melting point, 26—29°; I.V. 122; refractive index (27.5°), 1.465.

Soya-bean oil, raw or refined, should conform to the following requirements (A.S.T.M.):—*

	Maximum.	Minimum.
Foots, %	2.5	—
Loss on heating 105—at 110°, %	0.2	—
S. G. at 15.5°/15.5°	—	0.924
A. V.	5.0	—
S. V.	—	190
I. V. (Hanus)	—	128
Unsaponifiable matter %	1.5	—

Colour not darker than a freshly prepared solution of 0.1 gr. potassium bichromate in 100 c.c. pure H₂SO₄ (s.g. 1.84).

* *Amer. Soc. Test. Mats.*, U.S.A., 1922, D. 124, 22r, p. 749.

From the characteristics given above, soya oil will have a limited application in the paint and varnish industry. Its presence adds "flow" to a varnish mixing. It is stated to have a much greater wetting power with pigments than linseed oil and requires less power consumption during the grinding than when linseed paste is produced. Paste colours with soya oil as medium remain soft, and the same softening effect is noticed in varnish mixings. When blended with linseed oil, with the addition of suitable metallic driers, the results are satisfactory. The best drier for all forms of soya-bean oil is considered by J. A. Hongler⁵¹ to be a paste drier of cobalt-manganese. An oil compounded with this drier (the metallic content of the total oil being 0.1 per cent.) will form a skin in less than 8 hours and produce a hard film. The same oil using a lead linoleate drier of the same metallic content, takes over 40 hours to form a skin, and produces a film much softer than the oil containing cobalt-manganese paste drier. H. A. Gardner⁵² ("Papers on Paint and Varnish," 1920, p. 29) found similar results with a cobalt-manganese linoleate (0.03 per cent. Co and 0.07 per cent. Mn), but the drying time is given as 36 hours for the cobalt oil and 35 hours for the manganese oil. 0.5 per cent. lead as lead linoleate gave an elastic film in 42 hours on glass. A combination of cobalt manganese and lead, in the amounts of 0.01 per cent., 0.03 per cent., 0.20 per cent. respectively, gave an excellent film, drying in 18 hours and Pb, 0.2 per cent. and Co, 0.02 per cent. in soya oil gave like results. A mixture of 25 per cent. soya oil with linseed oil, using a manganese-cobalt-lead-drier to give a mixing containing 0.03 per cent. Mn, 0.01 per cent. Co, and 0.2 per cent. lead, gave films drying as rapidly as commercial boiled linseed oil containing 0.21 per cent. Pb and 0.041 per cent. Mn. It is advisable to blow the soya oil, with a previous heat treatment, before the addition of the driers, *e.g.*, the oil is heated to 600° F. for 30 minutes, the temperature is allowed to drop to 400° F. and then air blown in for 30 minutes. Cobalt, manganese and lead linoleates are added. The films obtained on drying are hard and smooth in the case of the cobalt and manganese, and elastic in the case of the lead. An oil made from 1 part bodied bleached soya-bean oil and 2 parts thinner, with the proper drier added, is said to make an exceptionally fine oil for flat whites or other flat paints. The characteristics of the blown oil have been studied by M. Toch;⁵³ and the constants of oil before and after blowing are as follows:—

	S. G. (15°).	Acid value.	Iodine value.
Original oil	0.9290	2.6	133
Blown oil	0.9630	1.9	105

A highly effective drier for soya oil is cobalt tungate. J. A. Hongler (*loc. cit.*) considers it to be an excellent oil for the manufacture of oil paints, as it will not liver or harden in the container. In general, the addition of a proportion, not exceeding 25 per cent., of soya-bean oil to linseed oil is unattended with detrimental results; it improves the flow of any mixing, but retards the hardening of the film. In some respects this retardation of hardening is an advantage. A comparison of driers for perilla, soya and menhaden oils will be referred to on page 81.

Para Rubber-seed Oil.—The great extension of the rubber plantations within recent years has brought into prominence possible uses of the seed and its expressed oil. The oil has been the subject of investigation, especially with a view to its use as a drying oil.⁵⁴ The Hevea rubber tree (*Hevea brasiliensis*) will produce on an average 500 seeds per annum (100 seeds weigh 360 grams). The cake left after extraction of the oil from the kernels is stated to be a valuable foodstuff for sheep or cattle, although it may have an appreciable hydrocyanic acid content—0.09 per cent. (Imperial Institute)—depending on the temperature of expression of the oil from the meal. The Ceara rubber seeds from Brazil weigh about 53.2 grams per hundred, but the seeds of *Funtumia elastica* from the West Coast of Africa are small, with thin, soft husks.

Dubosc⁵⁵ states that the seeds of *Hevea* contain 52 per cent. of oil and yield 33 per cent. in a single pressing, but this must refer to decorticated seeds, because R. J. Eaton⁵⁶ obtained 19.3 per cent. from the whole seeds, by extraction with a volatile solvent. The table on p. 65 gives a comparison of three varieties of rubber-seed oil with linseed oil.⁵⁷

The oil consists of 14 per cent. stearic and palmitic acid, 32.6 per cent. olein, 50.9 per cent. linolin and 2.5 per cent. linolenin.⁵⁸ Oil examined by the Amer. Soc. Test Matls. Committee, U.S.A., and obtained from the Produce Brokers' Co., London, gave the following values, which are an average of the results of six independent observers (*Proc. Amer. Soc. Test. Matls.*, 1922, 1, 367):—

S. G. (15.5°)	Acid V.	Sap. V.	I. V.	
			Hanus.	Wijs.
0.9249	5.89	193.3	136.9	138.7

The oil is not equal to linseed oil for paints and varnishes; its lead drying oil is slow drying and gives a soft film. Using a cobalt drier the result is also unsatisfactory, as shown in the following table, in which chia, rubber seed and sunflower are compared as drying oils. If the oil be heated with glycerine and calcium resinate

	Ceara manihot oil.	Fun- tumia.	Hevea brasiliensis.	Linseed.
Wt. of 100 seeds (grs.)	53.2	48	360	0.286—1.029 (East Indian).
Percentage of oil content of kernel	35	—	45.8	35.6—44.5 (East Indian).
Percentage of oil content of whole seed ...	15.75	31—33	22.25, 19.3	
S. G. 15°	0.9238	0.9320	0.9258	0.932
n_D^{15}	1.475	1.4788	—	1.4835
Relative viscosity	13	14.3	—	18
I. V.	135—137	138	131—138: 138.7	170—205
A. V.	0.625	2.65	5.26: 16.8	below 5
Percentage of liquid fatty acids	88.9	79.8	86	92.5
I. V. of liquid fatty acids ...	162.5	175.5	154.2	190—200

at 260° for 1½ hours, the acid value is reduced to 5.1, and the neutral mixing with a cobalt drier (sufficient to reduce the drying time of linseed oil to 6 hours) gives a film resembling that of soya, but inferior to that of linseed oil. The water-absorbing power and emulsification of the lead oil film are greater than that of a corresponding lead linseed oil film. Drying oils containing 3 per cent. lead oxide, made from linseed and Para rubber-seed oils, dry respectively in 5 hours and 7 hours, but the latter film holds a tack even after 4 days. The oil is suitable for soap-making, and can replace

Drying Experiments on Oils with Cobalt Driers.

	Setting time.		Drying time.	
	Hrs.	Min.	Hrs.	Min.
<i>Raw linseed oil with :—</i>				
0.3 per cent. Co	1	25	1	45
0.15 " "	1	35	2	45
0.09 " "	3	15	4	15
<i>Rubber-seed oil with :—</i>				
0.26 per cent. Co	3	15	not dry	
0.16 " "	4	15	after	
0.10 " "	4	15	2 days	
<i>Chia oil with :—</i>				
0.29 per cent. Co	0	45	1	15
0.18 " "	1	0	1	15
0.09 " "	1	15	1	35

	Setting time.		Drying time.
	Hrs.	Min.	
<i>Unrefined sunflower oil with :—</i>			
0.29 per cent. Co	1	45	not dry
0.14 " "	2	30	after
0.09 " "	—		2 days
<i>Refined sunflower oil with :—</i>			
0.32 per cent. Co	2	30	not dry
0.17 " "	3	15	after
0.09 " "	4	15	2 days

linseed oil in the manufacture of rubber substitutes. When blown at 250° for 5½ hours, it darkens appreciably and becomes very thick. It can be hardened by hydrogenation. To the varnish-maker Para rubber-seed oil stands in much the same position as soya oil, and at present seems to have no prospect of displacing linseed oil in general drying and protective properties.

R. J. Eaton (*loc. cit.*) concluded that it would be remunerative to import rubber seed into this country for crushing, especially as 1½ million acres are under rubber cultivation in Malaya. His estimate of the cost of shipping could be reduced by half if the seeds were decorticated before being shipped. The seed would probably cost from £9 to £10 per ton in this country. The quantity of seed available is now apparently satisfactory, and Eaton estimates that 26,000 tons of oil could be obtained annually from seed grown in the Malay Peninsula.

Two vegetable oils with marked drying properties have recently received considerable attention, viz., chia and oiticica oils.

Chia Oil.—The seeds of *Salvia hispanica*, a labiate, grow wild and are widely cultivated in Mexico, where they are known as chia or chian. Travellers carry the seed to mix with water, as it has been observed that the thirst is quenched with much less water when chia seed has been mixed with it; in this respect it resembles flax-seed tea. The chia plant grows to a height of 5–6 ft.; the seeds are oval in shape, about 0.5–1 mm. in diameter. The yield per hectare varies from 1000 to 4000 kilos. and, in certain parts of the country, two crops may be obtained annually. The seeds yield a yellow oil which is 30.5 per cent. of the weight of the seed expressed. The characteristics of the filtered oil are: S. G. (15°), 0.9338; acid number, 0.6; iodine value, 192.2; S. V. 192.2; unsaponifiable material, 0.8 per cent.; n_D (25°), 1.4885; hexabromide value of the fatty acids (Steele and Washburn method), 50.4, whereas perilla oil has the values 48–50.⁵⁹ The following figures were obtained by six independent observers:—⁸⁰

S. G. (15.5°)	Acid V.	Sap. V.	I. V.	
			Hanus.	Wijs.
0.9343	0.35	192.4	195.4	200.4

In the raw state the oil dries slowly. It exhibits more pronounced "creeping" than perilla oil, showing that chia oil has a high surface tension. It is advisable to heat the oil to 260° to remove this defect, and after this treatment it is stated to be superior to linseed oil, when treated with the same amount of drier. The comparison of chia oil with linseed oil on treatment with cobalt driers, is shown in a foregoing table (p. 65). When the oil is blown

at 250° for 6 hours, it is practically unchanged in colour and not very strongly bodied. From the comparison of wetting power with pigments, it would appear as if chia oil would yield more heavily-bodied paints than linseed oil. At present the supply of the oil is limited, but it is capable of development.⁶¹

Oiticica Oil.—The oil is extracted from the kernels of oiticica (a name applied to several species of *Moquilea* and *Conepia*, belonging to the *Rosaceæ*), indigenous in Brazil.⁶² C. Grimme⁶³ maintains that the tree from which the oil is obtained is named *Pleurogyne umbrasissima*. The kernels from *Conepia grandifolia* are 1 inch long and $\frac{1}{2}$ inch broad, and are stated to contain 62 per cent. of oil, semi-solid at the ordinary temperature (m. p. 21·5°, incipient fusion, 65°, complete fusion), consisting of a solid fat in a medium of liquid oil.⁶² C. Grimme (*loc. cit.*) describes oiticica fat obtained from *P. umbrasissima*, which begins to melt at 15·9° and fuses completely at 57°. The solidifying point is 15·2°. This fat appears to resemble that extracted from the kernels of *C. grandifolia*.

Oiticica oil resembles tung oil, yielding no solid hexabromide, and possesses a high specific gravity (0·9694), and an iodine value 179·5. It does not gelatinise when heated for 30 minutes at 250—270° in carbon dioxide, but when the temperature is raised to 300° coagulation ensues. At 100° it gains 4 per cent. in weight in air in 3 hours, and in 24 hours the total gain in weight is 4·5 per cent., whilst tung oil gained 2—3 per cent. under the same conditions.

The film produced is more uniform, transparent and continuous than that from tung oil. The melting point of the fatty acids is 53·7°—67°. One of the writers has found that cold benzol extracted only 29 per cent. of oil from the sliced kernels. The specific gravity of the oil varied from 0·94 to 0·9786 and the iodine value from 150 to 170. The oxygen absorption in 39 days gave an increase in weight of 7·38 per cent., whilst tung oil showed an increase in weight of 14 per cent. in the same period. The oil could be heated at 270°—280° without gelatinisation. An analysis of the kernels, after removal of the oil by benzol, gave the following figures:—

Moisture, 7·08 per cent.; oil, 17·35 per cent.; albuminoids, 11·07 per cent.; carbohydrates, 56·07 per cent.; fibre, 4·81 per cent.; ash, 3·62 per cent.

H. A. Gardner⁶⁴ obtained from oticia nuts 50 per cent. oil of acid value 45·3; I.V. (Wijs) 123; S.V. 203·2; n_D 1·49.

The potassium salt of the fatty acids obtained from the oil was very soluble in water and gave a crystalline acid, m. p. 98—99°, which was not elæostearic acid. The properties of the oil appear to be worth further investigation. It coagulates with difficulty on

heating, but it is partially oxidised so rapidly in the air that a crushing process is inapplicable, and extraction methods on a large scale have not as yet been successful. A systematic examination of the oil and its derivatives is required for success in extraction on a large scale. Reference has been made to the oil from *Pleurogyne umbra-sissima*, which resembles *oitica* in some of its characteristics, but its iodine value is given as 83.65, while the melting point of the fatty acids is 63°—68°.

There are a number of vegetable oils which are on the border line between drying and semi-drying oils. Some may be used directly as paint media, others require the addition of a considerable percentage of linseed oil before they can be so utilised in paints. They are essentially mixed glycerides containing small proportions of linolenin and larger amounts of linolin. Although several of the oils contain the same components, in almost the same proportions, yet the properties often differ widely as regards their use in special directions. The most interesting oils of the intermediate class are walnut and poppy-seed oils. A brief mention will also be made of safflower, sunflower, hemp-seed, fir-seed, cotton-seed, sesame, cameline, ravisson, colza and castor oils. The last is of special interest in connection with cellulose varnishes, because it is miscible in every proportion with alcohol, although it has no drying properties resulting from absorption of oxygen.

Walnut Oil.—Walnut or nut oil is obtained from the seeds of the common walnut tree, *Juglans regia*. The fruit must be allowed to ripen fully, and it is kept for two or three months before being pressed, because the fresh seeds yield a turbid oil which is difficult to clarify. The kernels contain 63—65 per cent. of oil (German 56.78 per cent., French 60.7 per cent.). The cold drawn oil is almost colourless, or of a pale yellowish-green tint, and has a pleasant smell with an agreeable nutty taste; the hot pressed oil is of a greenish tint with an acrid taste and smell. The oil is soluble in 88 parts of cold alcohol. The characteristics of the oil are shown in the following table:—

	S. G. 15°.	Solidify- ing point.	S. V.	I. V.	n_D^{40} .	Redwood visco- meter.
Crossley and Le Sueur	0.9259	27.5°	192.5	143.1	1.47054	231.8 secs. @ 70° F.
H.A. Gardner	0.925—0.9265	—	193.8—196	143—147.9	1.4770 (25°)	—

The composition of the oil is: glycerides of solid acids, myristic and lauric acids; of liquid acids, linolic and smaller quantities of oleic and linolenic acids. The formation of ether-insoluble bromoglycerides (1.42—1.9 per cent.) distinguishes it from poppy-seed oil.⁶⁵ The unsaponifiable matter of the oil is sitosterol.⁶⁶ Coffignier states that the proportions of the acids in the glycerides are oleic, 7 per cent., linolic, 80 per cent. and linolenic, 13 per cent. Walnut oil is stated not to yellow with time, when kept out of contact with light. The oil is mentioned in Pliny's "Natural History," but its introduction into painting followed that of linseed oil and preceded that of poppy-seed oil. Leonardo da Vinci gives directions for the treatment of the kernel preparatory to expressing the oil. By exposure of commercial walnut oil (yellow in colour) over water in the air the oil is bleached and shows the following characteristics: S. G. (15.5°) 0.9215; acidity, 2.3—2.4; I. V. (Wijs), 159—160; drying time of 8 ozs. drying oil, compared with an 8 oz. linseed drying oil, 6 hrs. Vasari mentions that walnut-oil film does not turn yellow. It is this property, combined with its slow setting, that has made walnut oil a rival of linseed oil as a paint medium. For ordinary paints the high price of walnut oil prevents its competing with linseed oil. The statement that paint films with walnut oil crack less than with linseed oil is not generally accepted.

Poppy-seed Oil.—The seeds of *Papaver somniferum*, *P. album* and *P. nigrum* contain 45—50 per cent. of oil, and are grown in Europe (N. France and S. Russia), Asia Minor, Persia, India and Egypt. They are largely crushed in N. and S. France to which the seeds come from the Levant and India, and also in Germany. The European and edible oil is known as "huile d'œillette," whereas the overseas seed yields oil known as "huile de pavot."

The cold-drawn oil from the first pressing is almost colourless (white poppy-seed oil). Expression at higher temperatures yields the much inferior red poppy-seed oil. The white oil has a pleasant taste and odour, does not rancidify, and is largely used as salad oil. The press cakes are a cattle food and in a mouldy state are a valuable manure, as they are rich in nitrogen. The characteristics of the oil are shown in the following figures:—

	S. G. 15.5°.	S. V.	I. V.	$\eta_D^{20^\circ}$.	Viscosity (Redwood).
Crossley and Le Sueur (E. In- dian oil)	0.9255—0.9268	189—196.8	133—137	1.4751	258.9—259.1 secs. @ 70°F.
Seeligman and Zieke	0.924 —0.927	189—198	140—160	1.477—1.478	—

The advantages and disadvantages of the use of poppy-seed oil in paints are discussed by Eibner.⁶⁷ As early as 1640 Wolffden stated that poppy oil dries throughout in 4 or 5 days, whilst linseed oil forms a pellicle. In 1644 Joseph Petitot considered umber to be the best siccative for poppy oil. The oil came into use in the seventeenth century, especially with Dutch painters, who appreciated its slow drying properties, and it was employed for whites, blues and pale tints. The knowledge of the oil dates from the time of Dioscorides before any mention was made of the use of linseed oil, but its application to painting followed that of linseed and nut oils. Carel van Mander in 1617 drew attention to poppy oil as an artist's medium. Artists favour the use of the oil, whilst decorators prefer linseed oil. Sabin is of the opinion that nut and poppy-seed oils yellow as much with age as linseed oil and require for their drying a large proportion of driers. A. P. Laurie (private communication) maintains that linseed-oil films rapidly darken in the light, while poppy-seed and walnut-oil films remain white. Observers have noticed that paint films containing poppy-seed oil show cracking with age, but the pictures of Rubens, Van Dyck, Teniers, Brughels and Wouvermanns show only slight cracking, although these artists are known to have used poppy-seed oil, and the oil is mentioned in mediæval recipes, just as linseed oil is, and it must have been freely used to give the hard insoluble films as found now.

If tempera colour be used as undercoating, then the permanence of the paint coating is good. The fault may lie in the use of poppy-oil undercoatings. Eibner (*loc. cit.*) has very carefully considered the "Frühsprungbildung" pointed out by E. Tauber in 1909.⁶⁸ Eibner lays stress on the following characteristics of a film of poppy-seed oil. It is slower and softer drying than linseed oil, and the oxidised films melt a little above 100°, whereas linseed-oil films carbonise about 260°. Oxidised poppy-seed oil is more easily soluble in solvents than oxidised linseed oil. In the oxidation of the oil more volatile matter is given off than in the case of linseed oil. The films show syneresis, indicating that the linoxyn is of a jelly consistency. Eibner considers the properties of the oil from the standpoint of composition and isomerism, especially in comparison with tung oil. The problem is an illustration of the limitations of chemical analysis in dealing with many of the peculiarities of drying oils. The oil examined by Eibner possessed the following characteristics :—

	A. V.	S. V.	I. V.	Oxy- acids.
Cold-pressed poppy-seed oil (3 weeks old)	3.6	197.5	133.5	0.78%

A very careful analysis established the composition of the oil under examination to be: α -linolic acid, 29.5 per cent.; β -linolic acid, 29.0 per cent.; oleic acid, 28.3 per cent.; saturated acids containing stearic acid,⁶⁸ 7.2 per cent.; glycerine, 4.2 per cent.; oxy-acids, 0.8 per cent.; unsaponifiable matter, 0.7 per cent. The acids were present as mixed glycerides and no free olein could be detected. Eibner considers that the high percentage of β -acid accounts for the slow drying of poppy-seed oil, on the analogy of the difference in activity between the α - and β -elæostearic acids.

The details of the investigation of the composition of poppy-seed oil are elaborate, but are on the same lines as those employed in the determination of the composition of linseed oil. There is much to be said in favour of the view that the amounts of isomeric unsaturated acids govern the physical properties of the oil film and that the nature of the mixed glycerides is also an important factor. Comparison of the characteristics of safflower oil with those of poppy-seed oil will show that further investigation of the composition of drying oils is required in order to understand the differences in their behaviour. Poppy-seed oil has not the keeping power of linseed oil; the glycerides are more easily hydrolysed and the acid value and oxy-acids increase on exposure of the oil. Linseed-oil films ripen more quickly than poppy-seed oil films, *e.g.*, after 40 days' exposure of the latter to the air the I.V. falls to 75.5, whereas in the case of linseed oil the I.V. had fallen to 8.7. In the course of his investigation Eibner discovered that, if the poppy-seed oil were thickened, the drying time of the paints was much reduced and the films showed no tendency to crack.

Pigment in 3 c.c.	Oil required.	Poppy-seed oil (drying time) on glass.	Thickened poppy-seed oil (drying time) on glass.
White lead	1.1 c.c.	6 days	1½ days
Zinc white	0.3	5 "	2 "
Ochre (natural)	1.4	6 "	2 "

Pigment in 3 c.c.	Poppy-seed oil on red lead poppy-seed-oil-colour (drying time).	Cracks form in	Poppy-seed oil thickened on thickened oil and red lead (drying time).	Cracks
White lead ...	2 days	1 day	1½ days	none
Zinc white ...	3 "	1 "	2 "	"
Ochre (natural)	3 "	2 days	2 "	"

Against this L. Barends showed in 1922 that sunflower oil, which has a composition approximating to that of poppy-seed oil, as far as is known at present, does not show this improvement in drying when it has been previously thickened.

For the decorator and varnish-maker its high price prevents it from being a rival of linseed oil. Colours are stated not to thicken or rivel so much, but they crack more than with linseed oil.

Safflower Oil.—This oil is obtained from the seeds of *Carthamus tinctorius* or *C. oxyacantha*, wild safflower, grown for edible oil and cattle cake (from decorticated seeds) in Bengal, Bombay, Hyderabad, in the driest areas of the Deccan and the Punjab, as well as in Egypt, Caucasus and Turkestan. The seed contains 31.6 per cent. of oil, but owing to the thickness of the husks, only 17—18 per cent. can be extracted by pressure. The husks are brittle and useless as food, since when present in large quantity in the cake they have an irritant tendency. The characteristics of the oil are as follows:—

S. G. 26°.	A. V.	S. V.	$n_D^{16°}$.	Reichert-Meissl value.	I. V.
0.914	0.6—0.78	177—203	1.477	0.2—0.5	116—150
0.9258 (15.5°)					

The oil consists of mixed glycerides of oleic, linolic and some linolenic acids. It is stated to possess fair drying properties,⁶⁹ but is not used in the paint and varnish industry. In India it is used as a protective for leather vessels, for Afridi wax cloth and for ropes exposed to the action of water, because when boiled in earthenware vessels for 2 hours it sets to a jelly (*rogban* or Afridi wax) in contact with water. The solidified product is probably the result of decomposition followed by polymerisation. The solid acids contain palmitic acid. Raw safflower oil with manganese borate requires 66 hours to dry. If the oil be heated to 186° in oxygen for 1 hour a very marked reduction in the drying time is obtained in the presence of manganese borate, but not with white lead.⁷⁰

Sunflower oil.—This oil is obtained from *Helianthus annuus*, which grows in Hungary, Russia, India and China. The Hungarian kernels contain 36—53 per cent. of oil, while Russian seeds contain 23 per cent. The pressed-cake is a valuable cattle food, containing 8—10 per cent. of oil. The oil is used for edible purposes in South Russia, and in 1906 50,000—60,000 tons of sunflower cake were produced in the N. Caucasus. The cultivation of the seed promises success in Cape Colony, where 3250 lb. of seed per acre is the yield of one crop.⁷¹ M. Bock⁷² states that the oil is used in the Russian varnish

S. G. 15.5°.	A. V.	S. V.	I. V. (Hanus)	$n_D^{25°}$.
0.924	7.5	189	124	1.4796

industry. The oil can be decolorised by earths at 120°, and it darkens when heated at 300° to produce a thickened oil.

* *Firseed Oil*.—This oil is obtained from the seeds of varieties of *Pinus*, e.g., *Pinus abies* (Norway spruce) and gives seeds yielding 31·6 per cent. of oil with the following characteristics :—

	S. G. 15°.	S. V.	I. V. (Wijs).	$n_D^{35°}$.
Pinaster seed oil ...	0·9312	192	120·5	1·4742

Pinus sylvestris (Scotch pine) gives seeds yielding 32·1 per cent. of oil.

	S. G. 15°.	S. V.	I. V. (Wijs).	$n_D^{35°}$.
Pine-tree oil, pine oil	0·9326	189·8	147·1	1·4704

Hemp-seed Oil.—The seeds of *Cannabis sativa* yield 30 per cent. of oil. France, Belgium, Germany, Northern Italy, Turkey, Algeria, India, Manchuria (yielding a low quality oil), Japan and North America are the sources of the oil. When fresh, it is of a clear yellowish-green colour, which darkens with age to brownish-yellow. The following characteristics show possibilities for use as a drying oil :—

S. G. 15°.	S. V.	I. V. (Wijs).	A. V.	$n_D^{25°}$.
0·925 } 0·931 }	190—191·8	148—155·7	3·9	1·4822

As a paint oil it is very much less in demand in this country than on the continent. The lower qualities are used for varnishes in Russia.⁷⁴ The sodium soap is too soft to be used as a hard soap. Its approximate composition is stated to be: mixed glycerides of linolic acid, 75 per cent.; oleic acid, 15 per cent.; linolenic acid, 15 per cent. (Bauer, Hazura and Grussner).

Niger Oil.—This oil is obtained from the seeds (achenes) of *Guizotia oleifera* from India, Abyssinia and E. and W. Indies. The fruits, which are of a lustrous black colour, contain seeds with 40—45 per cent. of oil, of pleasant taste and of yellow colour. The first crushing of the seed yields an edible oil. It is also used as a burning and soap oil. The following characteristics, as indicated by the iodine value, show its subsidiary drying properties. The oil film dries in 8 days, which may be shortened by the addition of siccatives to 16—20 hours.

S. G. 15°.	S. V.	I. V.	$n_D^{15°}$.	Viscosity (Redwood).
0·8738	188·9	126·6 }	1·4768	{ 263·1—292·6 secs. @ 70° F.
0·9248	192·2	133·8 }		

The films of the dried oil are dark and remain tacky for a long time. It is decidedly inferior to soya oil as a linseed oil substitute.

* (Huile de Pignon, Fichtensamenöl).

The following oils are worthy of passing mention, although they have very limited application as paint media.

Sterculia Oil (oil of Java olives) is obtained from *Sterculia foetida*, growing in the Dutch Indies, Malaya and Indo-China. The iodine value of the oil varies between 76.6 and 81.4. The reason for introduction here, among the list of drying oils, is that on heating to 240°—245° it gelatinises with spontaneous generation of heat.

Colza Oil.—Rape oil and ruben oil are intermediate between the semi-drying and non-drying oils. The following characteristics show the comparatively low iodine value: S. G. (15.5°), 0.9146 (crude), 0.9136 (refined); S.V. 173 (crude and refined); I.V. 106.8 (crude), 104.4 (refined). The oil yields 1 per cent. of solid fatty acids, which contain arachidic acid.⁷⁵ The other acids identified are erucic acid (I.V. 75) and rapic acid (I.V. 90), with indications of linolic and linolenic acids.

Ravison Oil.—Black Sea rape oil (*Brassica campestris*) is obtained from seeds growing side by side with those of flax. The seeds contain 33—40 per cent. of oil, which possesses stronger drying properties than those of colza oil. Rape-seed oil is an adulterant of linseed oil. S. G. (15.5°) 0.9183—0.9217; S.V. 177.9—179.3; I.V. 108.9—127.

Cameline Oil (Dodder Oil), *Myagnum sativum*, is also known as German sesamé oil, and is used to adulterate rape oil. When mixed with 50 per cent. of linseed oil and 10 per cent. driers it gives a drying mixture.⁷⁶ S. G. (15.5°), 0.926; S.V. 188; I.V. 135.3; n_D^{20} , 1.4761.

Sesamé Oil.—The oil is obtained from *Sesamum indicum* (white and yellow seeds, and *S. orientale* (red-brown to black seeds).

Fish Oils.—Oils may be obtained from all fish, the quantity varying with different species, the oil often predominating in a particular region of the fish. The main fish oils are those obtained from the menhaden, sardine, salmon, herring and dab, the lesser known being tunny, mackerel, pilcher, saith, whiting, sturgeon and sprat. Fish of the cod, skate, dog-fish, shark and haddock type give liver oil; the seal, whale and turtle yield blubber oils. Within recent years the fish-oil industry has made vast strides, as the result of experiments conducted by various Governments, notably that of India. In 1914 there were sixty-five factories producing oil and guano from fish, mainly from the Indian sardine (*Clupea longiceps*). The crude native method of oil extraction, where the fish was allowed to putrify and the exuding oil collected, is being replaced by the more modern method of boiling in cauldrons, skimming the oil away and drying the residue for use as a fertiliser. Latterly

there has been a demand for a finer grade oil for the fat industry, and in some cases for conversion into edible products. The use of fish oils for soap-making is attended with many difficulties, due to the persistent odour, but claims have been made that all taste and odour can be eliminated on hardening by means of catalytic agents. Müller⁷⁷ found, after conducting a number of feeding experiments on human beings, that hardened whale oil, m. p. 36° , is an efficient substitute for animal fats. The principal areas of the fish oil industry are: the east and west ports of America and Canada, Japan, India, Norway and to a lesser extent Great Britain (*Chem. Trade Journ.*, 2/6/1922).

The largest area of the American fish oil industry is in the Chesapeake Bay district, which contains about fifty factories. The fishing operations are conducted during eight months of the year, the chief catch being the menhaden fish, which contains about 4 per cent. of oil. During 1920, the average amount of oil obtained was 6 gallons per 1000 fish, the year's production being over 10 million gallons. In 1919, 5,415,600 gallons of oil, 15,103 tons of dried scrap and 47,915 tons of acidulated scrap were obtained.⁷⁸ The menhaden or moss-bunker is a small, bony, inedible habitant of the coast waters of the Atlantic Ocean from Texas to Maine. These fish originate in the warm waters of the Gulf of Mexico and the Caribbean Sea, travel northward in great schools as the summer progresses and return to the south in the winter. The fishing season, following the movement of the school, begins in April and continues until the cold weather sets in. The production of oil from menhaden (*Alosa menhaden*) is worthy of detailed treatment, because of its use when mixed with linseed oil as a paint medium, although the oil itself never dries permanently hard, and has a tendency to become soft in a warm, moist atmosphere; moreover, its smell is undesirable, although the fishy odour is stated to be removable by catalytic treatment.⁷⁹

During the early years of the nineteenth century, menhaden was used as a fertiliser only, but the value of the oil was soon discovered. The method of extraction consisted in placing the fish in open boxes, covering them with water and pressing the mass with weighted boards, under which disintegration took place and the oil was liberated and floated to the surface. The introduction of the process of cooking by steam, which caused more rapid disintegration and increased yield of oil, gave importance to the industry. The necessity of cooking and pressing the fish while they are relatively firm and solid, in order to obtain a maximum yield and a satisfactory

quality of oil, is now fully recognised. On the eastern seaboard of America in 1920 there were sixty factories in operation, served by a fleet of 150 steamers and employing 7000 men. The steamers leave their berths in the early morning and put back to their home factories, or into the nearest harbour, at dusk, so that the cooking of the fish may be started before it begins to deteriorate. The cooking is done in a large cylinder, about 2 ft. in diameter, equipped with a screw conveyor that slowly forces the mass through the cylinder, while heat is being applied by means of steam jets in the bottom. The soft wet mass is then conveyed to the presses, which consist of a tapered screw rotating inside a similar and parallel shaft called the curb. The mass moves forward and is pressed by the decreasing size of the screw and curb. It is subjected to steam pressure during its travel and drained both internally and externally.

Oil and water are caught in concrete basins beneath the presses and carried to receiving tanks for further treatment, while the remaining solid matter or scrap is deposited separately, dried, treated with acids and sold as fertiliser. Each press has a capacity of 100,000 fish per hour, and in each 100 lb. of material leaving the presses there are approximately 4 lb. of oil, 46 lb. of water and 50 lb. of scrap. The separation of the oil from the water is accomplished by means of a series of open tanks, each connected to take the overflow or skimmings from the preceding tank in the series, so that, when the fluid has reached the last tank, it is practically free from oil. After separation has been accomplished, the oil is heated to the boiling point for about 30 minutes, and then, after being allowed to stand for several days, and exposed to the rays of the sun, it is run into storage tanks.

Both quality and yield of the oil depend primarily on the quality of the fish, which varies with the locality in which the catch is made, the season and the year. The best oil is obtained from the large flat fish, which are found usually in northern waters towards the end of the fishing season, and a yield of 8 gallons of oil per thousand fish is a fair average, though this figure is exceeded under favourable conditions. The quality of the oil also depends on the skill of the handlers at the factory, and the promptness and thoroughness with which the cooking and pressing are accomplished. During recent years the fishermen have begun to realise the necessity of producing not only as much oil as possible per unit of fish, but also an oil of good quality, as determined by its colour, odour and clearness. The output of these seaboard factories

is the crude oil of commerce, delivered to the refiners in tank cars or barrels.

Refining Menhaden Oil.—The treatment to which the crude oil is subjected by the refiner is a continuation of the process carried on at the fish factory. It consists primarily in heating the oil to a fairly high temperature and then slowly chilling it, in order to allow the solid matter to congeal and separate from the oil. This is accomplished by drawing the oil from the storage tank into steam-jacketed kettles, where it is heated for a period of about 6 hours to a temperature of 170° F., during which time it is constantly agitated, either by air or by mechanical means. This drives out the moisture and dissolves the crystals or foots, which are formed in the oil during its stay in the storage tank.

The oil is then drawn off into cooling pans and allowed to stand 3 or 4 days, subject to a gradual reduction in temperature. The cooling is done by means of pipe coils, with which the pans are equipped, and through which a circulation of cold water or brine is maintained. As the temperature of the oil falls the foots separate from it and remain in suspension until the oil is ready for filtering. Filtration consists in straining the oil through canvas bags hung on wooden racks. The chilled oil is run by gravity into the bags, through which it drains into the pans below, the foots remaining inside the bags. The oil so collected is the first run of refined oil, and its quality depends on the temperature at which it is strained. The foots are subjected to a pressure of about 3000 lb. in a press for a period of 8—10 hours. The oil thus separated from the foots is known as hydraulic oil because of the type of press used. Its quality depends on the temperature at which it is pressed. During recent years attempts have been made to separate the oil and foots by centrifugal force, but the result has not been entirely satisfactory. The ordinary straining and pressing process still continues to stand alone in producing a uniformly reliable, low cold test oil, free from moisture and foreign matter. The oil so obtained should show a cold test of from 30° to 32° F., and possess the following characteristics:—

A.V., 3.64; S.V., 196.5, 188.7; I.V., 188.5; S. G. (15°), 0.9307; cold test, 28° F. (solidifying point); flash point, 513° F.

The oil obtained from the first straining through the canvas bag usually shows a better cold test than the hydraulic oil.

Bleaching and Blowing the Oil.—The refined oil, as obtained from the straining and pressing processes, is stored in closed tanks. If a particularly light-coloured oil, or one with a high viscosity, is

required, it may be bleached or blown, or both. Bleaching is accomplished by filtering the oil with fuller's earth, or by cooking it with an alkali. In the fuller's earth process, oil is mixed with the earth and forced through a horizontal filter-press, consisting of a series of canvas sheets hung vertically between perforated metal plates, so that the clear oil runs through perforations into adjacent pans, while the compressed earth and foreign matter adhere to the canvas sheets. This has the effect of lightening the oil several shades in colour and also clarifying it to a considerable extent. In the alkali process the oil is mixed with caustic soda and subjected to heat in an open kettle. A low acid oil is usually treated by filtration in order to bleach it, and a high acid oil is treated by the alkali process in order to produce soap. In the latter case the resulting bleached oil is separated from the soap by skimming it off the top, and the quality of the oil is equal to that obtained from the filtration process, but it is less in quantity. The bleached oil is allowed to stand in shallow pans for several days, exposed to heat and sunlight to remove the last traces of moisture and to complete the bleaching.

Blown Fish Oil.—Blown fish oil is obtained by forcing a strong current of compressed air through the oil, in a special tall tank of relatively small diameter, which is steam-jacketed and provided with a ventilator arranged in the top of the tank. The tank is filled with oil, which is gradually heated to 110° F., and agitated by compressed air entering below the oil. The agitation or blowing is continued until the required viscosity or gravity is obtained. If the oil reaches a temperature of 230° F. it takes up oxygen very rapidly, so that it is easy to over-oxidise the oil and produce solidification. During the process there is an increase in the acidity and depth of colour of the oil, which, however, is partially deodorised and undergoes a shrinkage in volume.⁸⁰

Fish Oil Fats.—Approximately 10 per cent. of the crude oil is obtained in the form of fats. The fats from the "hydraulic" oil are bleached with caustic soda, yielding a hard, white, silky substance known as bleached fish fats or fish stearin, which is used for soap and is a component of greases. The demand for refined fish oil products equals the supply in an average year, but there is no fixed relation between the demands for refined fish oil and the demands for the by-products, fats and soap.

Reference has been made to the defect of the oil in failing to produce a permanently hard surface on oxidation. For general outside work, especially on the sea coast, and for application on hot surfaces, it is suggested that a mixture of menhaden oil with

linseed oil up to 75 per cent. of the former might be employed. Toch ⁸¹ recommends its use in paints for structural steel and other metals. Any of the standard driers can be employed, but cobalt linoleate is considered as the most effective. An advantage claimed for the oil in combination with linseed oil, is that the mixture is more impermeable to the action of water than linseed oil alone; this may be due to the bodying which is brought about during the refining of the oil, and a truer comparison ought to be made with thickened linseed oil. Another advantage claimed is that it has the power, when dry, of giving a film of great heat-resisting power. Hence it has been recommended for use in smoke-stack and boiler paints. Undoubtedly the mixture of fish oil and thickened linseed oil possesses good heat-resisting powers. In reference to the technology of other fish or marine oils, the extraction from herring, sardine, salmon, sprat, etc., is conducted essentially in the same manner as described under menhaden oil (for details vide *Chem. Trades Journal*, 2/6/1922). For the extraction of high-grade oils (e.g., cod-liver oil industry) special precautions have to be taken. The oil is extracted *in vacuo* at 90° F., and filtered *in vacuo*, whereby the odour is much reduced. In some American factories the livers are primed for 48 hours with salt water, which disintegrates the cells. ⁸²

Blubber oil from the whale, seal or turtle is obtained by boiling the blubber after separation of the flesh. Whale oil is obtained chiefly from the Greenland whale (*Balaena mysticetus*), which yields 180 barrels per animal. Norway has the largest annual output, amounting to over one million gallons.

The offensive smell of fish oils generally is considered by some to be due to the presence of aliphatic amines with other nitrogenous and phosphorus compounds (oil from fresh livers of shark and dog-fish are free from nitrogen, of fairly light colour and unobjectionable odour). Others consider that clupanodonic acid oxidation products are the cause. The evidence is strongly in support of the formation of volatile decomposition products, in spite of the results shown in the graph on p. 42. The following characteristics of varieties of fish oils are of interest :—

	S. V.	I. V.	n_D^{20} .
Menhaden oil	191.2	151.7	1.4778
Salmon oil	185.0	137.2	1.4768
Herring oil	186.5	139.8	1.4765
Sardine oil	187.3	158.1	1.4791
Cod oil	186.9	151.0	1.4770

Twitchell⁸³ gives the following composition for menhaden oil: palmitic acid, 22.7 per cent.; myristic acid, 9.2 per cent.; stearic acid, 1.8 per cent.; unsaturated acids (16 carbon atoms), none; unsaturated acids (18 C.), 24.9 per cent.; unsaturated acids (20 C.), 22.2 per cent.; and unsaturated acids (22 C.), 20.2 per cent.; unsaponifiable matter (cholesterol), 0.6—1.43 per cent. Owing to the presence of cholesterol, the oil is slightly optically active. Reference must be made to the later work of J. B. Brown and G. D. Beal on p. 43.

Japanese Sardine Oil is worthy of mention in connection with an investigation by A. Eibner and E. Semmelbauer.⁸⁴ According to them, the following composition is to be assigned to Japan sardine oil: clupanodonic acid, 12.7 per cent.; linolenic acid, none; α -linolic acid, 9.8 per cent.; β -linolic acid, 10.1 per cent.; oleic acid, 28.6 per cent.; oxy-acids, 8.7 per cent.; saturated acids, 22 per cent.; glyceryl, 4.1 per cent.; cholesterol, 0.5 per cent. The details of the analytical work establishing the above figures are closely related to those given in connection with the composition of linseed and perilla oil. A comparison of their methods with those of Brown and Beal previously referred to is of interest. The latter two investigators have very carefully examined the many highly unsaturated acids present in menhaden oil. In sardine oil, as examined by Eibner, a decabromo-acid, corresponding to Tsujimoto's clupanodonic acid ($C_{22}H_{34}O_2$) was successfully isolated, and the reduced decabromo-acid gave a 99 per cent. yield of decabromo-acid on rebrominating. The absence of linolenic acid was proved by the insolubility of the bromo-acids (solid) in benzol. In spite of the presence of highly unsaturated glycerides, the percentage of non-drying fats is too high to permit normal drying of the oil. The glycerides present were found to be oleodipalmitin and dipalmitostearin and mixed glycerides of the other acids. C. Grimme,⁸⁵ in an examination of the herring-oil fatty acids, concluded that the acids present were: saturated, 20 per cent.; oleic, 20 per cent.; linolic, 33 per cent.; linolenic, 17 per cent.; clupanodonic, 9 per cent.

Among the *Blubber Oils* Milligan, Knuth and Richardson⁸⁶ have determined the composition of whale oil. The original sample had the following constant: I.V., 121.6; mean molecular weight of fatty acids, 277; solid acids, 16.7 per cent.; I.V. of the solid acids, 5.6. The lead salts of the solid fatty acids were precipitated from the mixed fatty acids in alcohol, and the lead soaps recrystallised from alcohol. From the alcoholic solution the liquid acids were obtained in the usual way. Both solid and liquid acids

were methylated separately and the methyl esters fractionally distilled at a pressure of 7.9 mm. The solid acids contained myristic, 13.6 per cent., palmitic, 68 per cent., stearic, 16.8 per cent.; higher unsaturated acids, 1.6 per cent. As regards liquid acids it was calculated that the composition of the methyl esters was: C₁₄ acids, 2.7 per cent.; C₁₆, 15.4 per cent.; C₁₈, 42.7 per cent.; C₂₀, 20.2 per cent.; C₂₂, 15.4 per cent.; C₂₄, 2.8 per cent.; and unsaponifiable, 0.7 per cent. In seal oil K. H. Bauer and W. Neth⁸⁷ found 13.3 per cent. of insoluble bromides which they stated were derived from clupanodonic acid.

The use of fish oils, other than menhaden and sardine oils, in paint manufacture is generally unsatisfactory, and as they are in demand for other purposes, *e.g.*, leather dressings, there is no advantage in their employment, unless there is a shortage of linseed oil, when they may be used in admixture therewith. Their smell and dark colour are serious disadvantages. It is very difficult to deodorise any of the fish oils except by hydrogenation, which lowers the iodine value and reduces the drying properties, besides increasing the viscosity. H. A. Gardner⁸⁸ recommends the addition of 5—10 per cent. of pine oil to fish oils. Heat treatment, especially in the presence of driers, reduces the odour. G. Weiss⁸⁹ claims that the oils may be deodorised by treatment with a fine jet of steam in the presence of alkali. Paints, made with suitable proportions of menhaden, soya and linseed oil, with or without varnish resins and the usual driers, have yielded results which are stated to be equal or even superior to those produced with linseed oil alone.⁹⁰ The wearing values of paints made with menhaden and linseed oil (100 : 50 : 25 per cent. of menhaden oil) and white lead and zinc white are satisfactory, but those containing 100 per cent. of menhaden oil are, and remain, very dark in colour. Blown herring oil has proved a serviceable constituent of heat-resisting paints and for counteracting the corrosive effects of sea air.

The results of the examination of the properties of fish oils show that the presence of a high proportion of unsaturated acids, or even of highly unsaturated hydrocarbons, does not give to the oil properties which are of great practical value for use as a drying oil. Many fish oils show iodine values from 132 to 151, but possess only slight drying properties, whereas vegetable oils with iodine values as low as 120—130 (cotton seed, soya bean, etc.) are capable of being dried in a relatively short period of time. The importance of considering all the components and their inter-relationship is well

manifested, and further investigations on the lines of Eibner's work are very desirable.

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CHAPTER III

THE OXIDATION OF DRYING OILS

In any discussion on the oxidation of drying oils, all their components must be considered, and it is advisable to point out the action of oxidising agents on these. Beginning with the solid and saturated acids of any vegetable drying oil such as linseed oil, stearic and palmitic acids are the most important, although small quantities of arachidic, $C_{20}H_{40}O_2$, and myristic, $C_{14}H_{28}O_2$, are sometimes present. Oxidation by alkaline potassium permanganate produces acetic, butyric, caproic, $C_6H_{12}O_2$, oxalic and adipic, $C_6H_{10}O_4$, acids; whilst stearic acid yields dibasic acids, succinic and adipic, and normal valeric acid, $C_5H_{10}O_2$.

Dakin¹ found that when the ammonium salts of saturated fatty acids with a large excess of 3 per cent. hydrogen peroxide were heated to boiling, ketones were produced in small quantities, especially in the case of the higher acids, *e.g.*, stearic acid gave quindecylmethylketone, $C_{15}H_{31}COCH_3$, whilst butyric acid, $C_4H_8O_2$, gave acetone, CH_3COCH_3 . H. E. Fierz-David² states that he has obtained volatile ketones from cheese by the oxidising action of *Penicillium glaucum* on the fats present.

Treatment of the unsaturated acids of linseed oil with alkaline potassium permanganate furnishes hydroxy-acids, in which the hydroxyl groups have been introduced where the ethenoid linkages occur, *e.g.*, oleic acid gives dihydroxystearic acid, $C_{17}H_{33}(OH)_2COOH$, together with the simpler dibasic acids, *e.g.*, azelaic, $C_7H_{14}(COOH)_2$ and oxalic acid, and nonylic acid, $C_9H_{18}O_2$ (pelargonic acid). Under special conditions of oxidation with potassium permanganate, keto-hydroxystearic acid, $C_{17}H_{32}O(OH)COOH$, is produced. If linolic and linolenic acids be subjected to the same treatment, hydroxy-acids are also produced, the number of hydroxyl groups being determined by the number of ethenoid linkages, *e.g.*, tetrahydroxystearic acid, $C_{18}H_{32}(OH)_4O_2$ (sativic acid), is obtained from linolic acid, but several forms of this acid exist. In the case of linolenic acid from linseed oil Hazura obtained two isomeric acids, linusic (linusinic) and isolinusic, but no evidence for the existence of two forms of linolenic acid in the oil can be based on their production, in spite of the result obtained by K. H. Bauer⁸⁶ (*cf.* Chap. I), who isolated linusic acid from the oxidation of the so-called β -linolenic acid.

The action of ozone throws much light on the structure of the component acids of linseed oil (*cf.* p. 39).

Harries, and independently Molinari, examined the action of ozone and ozonised air on solutions of the unsaturated acids in hexane. The absorption of the ozone to give an ozonide is quan-

titative: $\text{CH}_3(\text{CH}_2)_7 \begin{array}{c} \text{CH} \text{---} \text{CH} \\ | \quad | \\ \text{O} \text{---} \text{O} \end{array} (\text{CH}_2)_7 \text{COOH}$, oleic acid ozonide.

Under special circumstances perozonides are formed.

The ozonides are decomposed by hot water to yield aldehydes, dibasic acids and semi-aldehydes of dibasic acids, *e.g.*, from oleic acid ozonide, nonylic acid, nonylic aldehyde, azelaic acid, and the semi-aldehyde of azelaic acid are obtained (p. 39).

The formation of nonylic and azelaic acids indicates the formula $\text{C}_{18}\text{H}_{32}\text{COOH}$ (9 : 10) for oleic acid (p. 32).

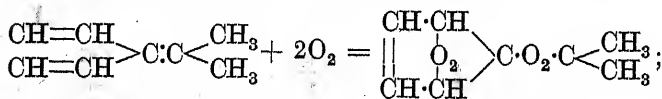
Erdmann, Bedford and Raspe³ obtained ozonides of linolenic acid, which on decomposition yielded propionic aldehyde malonic acid and semi-aldehydes of malonic and azelaic acids, *cf.* p. 39.

The action of ozone on China wood oil acids gives valerianic, azelaic and succinic acids (*cf.* p. 36).

It is evident that valuable information, as to the composition of the drying oil acids is obtainable from the study of their oxidation products. Molinari has shown that polymerisation of aldehyde products occurs, *e.g.*, nonylaldehyde ($\text{C}_9\text{H}_{18}\text{O}$) changes to paranonyl-aldehyde, and such polymerisation products are usually stable. Further reference to polymerisation will be made in connection with the study of the products in the drying process of oils.

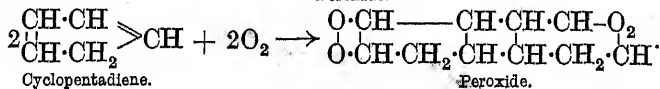
From the general properties indicated by the constitutional formulæ, it may be presumed that the oxidation of the drying oil will proceed in stages, a molecule of oxygen becoming attached where there is an ethenoid linkage. It is generally agreed that the glyceryl group is not attacked during the first stages of the oxidation. The absorption of oxygen by drying oils is slow compared with the action of oxidising agents mentioned above, and it depends on conditions of temperature and of illumination. Peroxides of the type $\begin{array}{c} \text{O} \text{---} \text{O} \\ | \quad | \\ \text{C} \text{---} \text{C} \end{array}$ are formed primarily from the linolenic and linolic

glycerides, and to a very small degree from olein. It is quite easy to show the peroxide formation by means of the reaction with potassium iodide in acetic acid solution, whereby iodine is liberated. Many instances of absorption of molecular oxygen occur, *e.g.*, the oxidation of dimethyl fulvene and of cyclopentadiene may be illustrated by the following equations:—



Dimethylfulvene.

Peroxide.

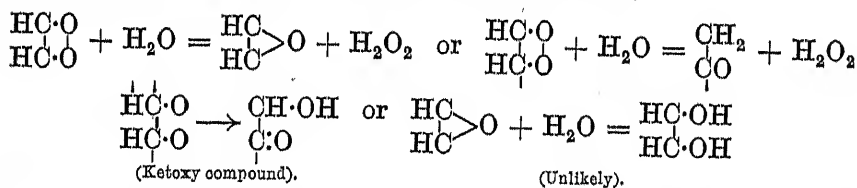


Cyclopentadiene.

Peroxide.

In the latter case, polymerisation occurs during oxidation. H. Wolff has stated that, when sheets of paper soaked in linseed oil are pressed to form a compact block, the outer layers are found to consist chiefly of oxidised oils and the inner layers of polymerised oil. Prolonged drying diminishes the degree of difference between the layers with respect to the proportion of oxidised fatty acids.⁴

Which of the double linkages absorbs oxygen first is not definitely known. In the cerium salts of β -elæostearic acid the absorption proceeds in two stages, the 9 : 10 carbon atoms being first attacked. Ingle considered that the ethenoid carbon atoms, adjacent to the COOH group, are prevented from absorbing halogens from a strongly acid solution; moreover, the iodine value of crotonic acid is negligible compared with that of oleic acid. It would appear that the closer the ethenoid linkage is to the carboxyl the less the tendency to absorb oxygen. Nevertheless, the rancidity of drying and non-drying oils is due to the escape of volatile aldehyde products split off from the carbon chain remote from the carboxyl grouping. The only crystalline glyceride of a drying oil β -elæostearic glyceride is oxidised very rapidly in the air to yield a colourless peroxide, infusible at 230°. ⁵ It is decomposed by water, with the formation of a yellow, spongy solid and hydrogen peroxide. The action may be represented by the following schemes (Fahrion):—



It is possible that the yellowing of linseed oil or highly unsaturated oil films may be explained by the formation of a similar oxide or ketone; moreover, linolenic and clupanodonic acid have been shown by Eibner (*loc. cit.*) to produce coloured films. As far as the investigation of the amount of oxygen absorbed and the changes in weight during absorption under varying conditions of temperature, concentration of aqueous vapour and quality of light are concerned, much work has been done, and the results are to be found in most text-books. The table on p. 88 may be taken as typical, and the graphs illustrate the changes in weight when four chief drying oils are exposed to air.⁶

In the presence of a drier or catalyst, the induction period at the commencement of the curve is absent.

When the oil film is dry there is a position of equilibrium where

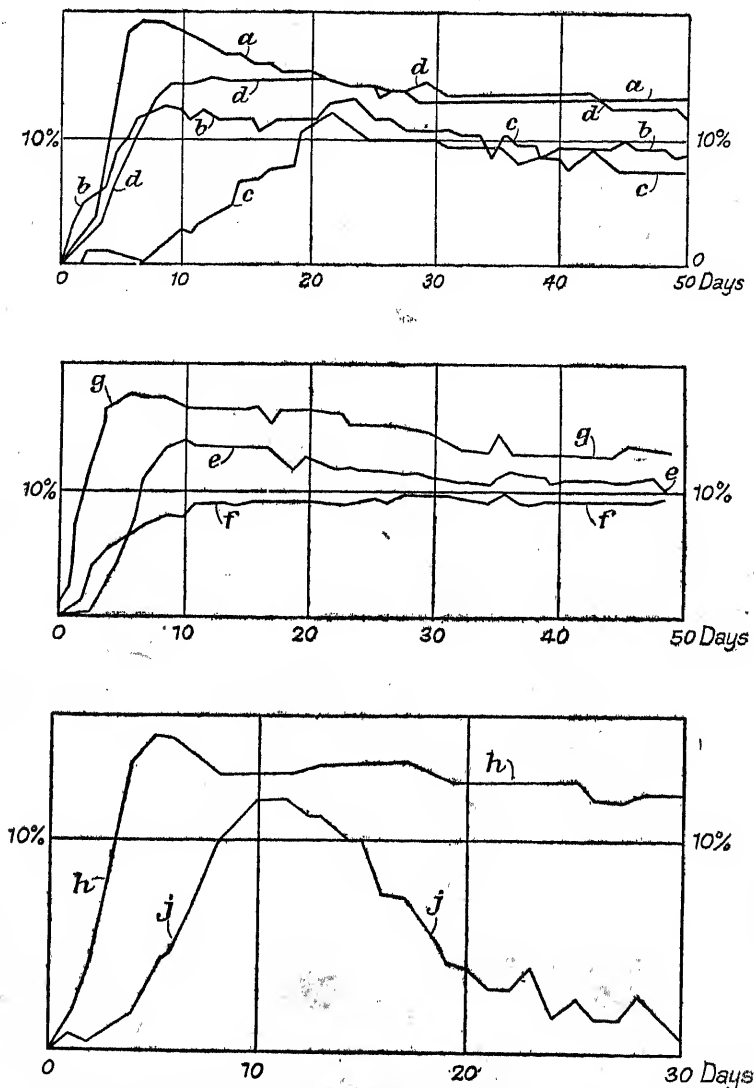


FIG. 3.—Percentage Gain in Weight on Exposure to Air of Drying Oils (Eibner).

a = Perilla Oil; *b* = Soya Bean Oil; *c* = Hemp Oil.
d = Chinese Wood Oil; *e* = thin Standoil; *f* = thick Standoil.
g = Plate Linseed Oil; *h* = 7-year-old Linseed Oil; *j* = 21-year-old Poppy Oil.
 Perilla Oil, 32.1% of max. increase in weight lost after 60 days' exposure.
 Soya Oil, 30.4% " " "
 Hemp Oil, 46.2% " " "
 Chinese Wood Oil, 14.4% " " "
 Thin Standoil, 24.8% " " "
 Thick Standoil, 8.0% " " "
 Plate Linseed Oil, 22.8% " " "
 Poppy Oil, 100% " " "

Condition of oil. Temp. 15°, approx.	Increase in weight. %	Density at 15°.	Increase in density. %	Increase in volume. %
<i>Linseed oil :</i>				
Liquid	0	0.93179	0	0
"	2.08	0.94850	1.8	0.28
"	5.83	0.97696	4.8	0.87
Thick frothy liquid	9.66	1.00123	7.4	2.06
Tacky	14.14	1.0424	11.9	2.0
Just set	17.34	1.0582	13.6	3.3
Solid linoxyn	17.90	1.0656	14.3	3.1
" "	18.57	1.0902	17.0	1.35
" " 3 months old	10.3	1.1054	18.6	—7

the gain in weight, due to oxygen absorbed, is equal to the loss in weight due to escaping vapours and gases. The observed nett gain in weight of a film is less than the weight of oxygen absorbed, owing to losses due to volatile matter.

Genthe⁷ found that linseed oil, which absorbed 22.6 per cent. of oxygen under ordinary conditions, would absorb 25.8 per cent. when exposed to the light of a mercury vapour lamp; whilst at 95° the gain in weight in air corresponded to an absorption of 26.8 per cent., and in an atmosphere of oxygen the absorption was 34.7 per cent. There is a maximum increase in volume at the setting point of the oil, and a contraction with increase in density after 3 months, the contraction being accompanied by a loss in weight which varies with the drying oil. The differences between the losses in weight (Schwundbetrag) of the dried oils are shown in the graphs on p. 87. The behaviour of clupanodonic acid compared with linolenic, linolic and oleic acids is very marked. Sabin⁸ gives figures showing a final shrinkage of 13.4 per cent. with a total gain in weight on the original linseed oil of only 2 per cent. More attention ought to be paid to these figures of volume and weight changes of linseed oil films, because they are factors connected with the durability of drying oil coatings. The defects (Eibner) of cracking, noticeable in both oil and resin films, are often caused by neglect of the volume changes subsequent to the setting of the film and to the production of surface strains. In the presence of moisture, the oxidation of drying oils proceeds in a somewhat different manner. The oxidation of linseed oil in the presence of moisture-saturated air has been investigated by several workers, and the results may be summarised as follows:—

De Waele⁹ concludes that the decomposition of the peroxide primarily formed is initiated by moisture; and that equilibrium conditions, *i.e.*, decomposition *versus* back pressure, are attained by

interpretation of the latter as pressure of water vapour. H. A. Gardner¹⁰ has investigated the changes in the weight of oil films, containing 0.2 per cent. of a metallic oxide as catalyst, exposed to moist air and to dried air in a special apparatus. The results show that in every case there is a great increase in weight during the first 24 or 48 hours. The films dried in moist air almost invariably showed a gain in 24 hours, which was equal to that shown by the same films in dry air in 48 hours; this gain was followed by a decrease, in some cases amounting to almost more than the original

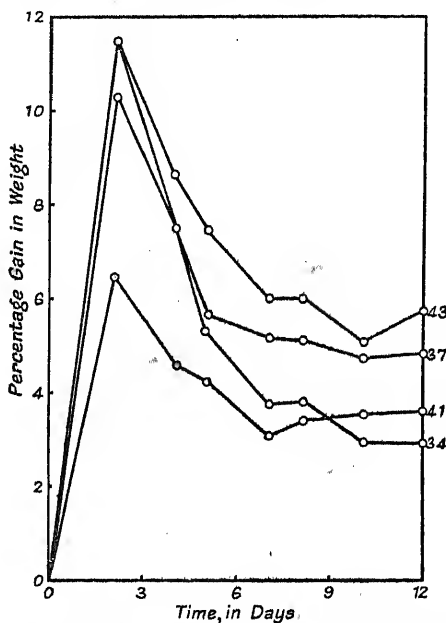


FIG. 4.—Linoleate driers (dry cabinet). 34. Al linoleate. 37. Zn linoleate. 41. Co linoleate. 43. Pb linoleate.

gain. Later on, and in the majority of cases, the weight increased again, and a second maximum was reached before the oil settled down to constant weight. The second maximum was particularly noticeable in those cases in which drying occurred in a humid atmosphere, it being often greater than the first maximum. In dry air the second rise is usually slight and sometimes entirely lacking. The final hardening of the film is reached more quickly and directly in dry air than in an atmosphere saturated with moisture. In the presence of moisture there is a second rise in the weight-time curve. The decrease in weight is said to be due to the decomposition of peroxide and to the escape of volatile products; the second rise in

the curve is due to a reaction of the glycerides and water (see Figs. 4 and 5). The water taken up in the secondary period is chemically combined, since it is not given up when exposed to dry air. The second decrease in weight is held to be accounted for by the decomposition of glycerol into volatile decomposition products. Gardner's statement that it is quite generally believed at the present time that, at some stage during the drying of the oil, the fatty acids separate from the glycerine with which they are combined, is open

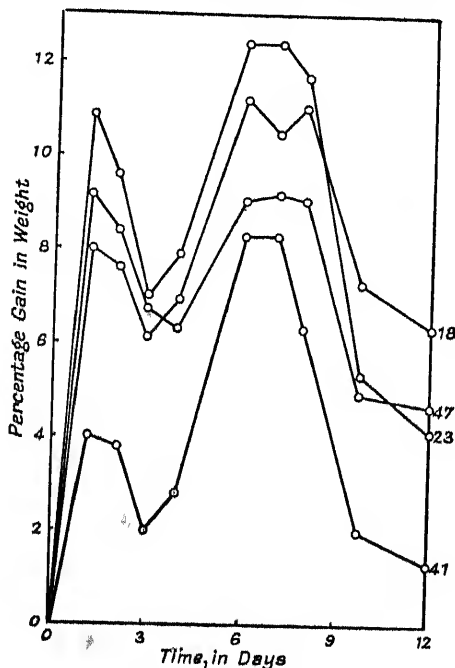


FIG. 5.—Linoleate driers (moist cabinet). 18. Al linoleate. 23. Zn linoleate. 41. Co linoleate. 47. Pb linoleate.

to criticism, although from one of the authors' experience the acidity (water soluble) of varnish films increases on exposure to air under ordinary conditions, but whether from decomposition or hydrolysis is unknown. Moreover, glycerine is hardly attacked by hydrogen peroxide, except in the presence of iron salts, or by oxygen except in the presence of uranyl sulphate as catalyser.¹¹ *

The most recent investigation of the changes in weight accompanying the oxidation of linseed oil is that of F. H. Rhodes and A. E. van Wirt.¹² The form of apparatus used by them, in an investigation on the oxidation of linseed oil and of paints, is shown

* The emulsifying of the metallic linoleates will tend to increase the apparent gain in weight of the films due to water absorption.

in Fig. 6. The experimental method embodies that of earlier workers. In Fig 7 are shown the time curves of linseed oil with and without driers, as well as the volume time curves of the volatile products of the oxidation. At the temperature (30°) of the experiments, the volume of the volatile products appears to be greater than in the earlier graphs, drawn from observation at the ordinary temperature. Rhodes and van Wirt examined the influence of pigments on the drying time of linseed oil. The presence of silica (silex) showed no accelerating action, but reduced the period of induction and caused a retarding action, due to increased thickness of the film, with a decreasing rate of diffusion of oxygen. The

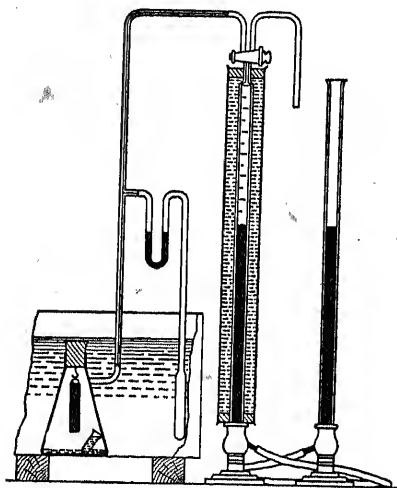


FIG. 6.—Apparatus for Determination of Oxygen Absorption of Linseed Oil and Paints (Rhodes and van Wirt).

presence of lithopone, titanox and leaded zinc retarded the rate of oxidation and also reduced the volume of oxygen absorbed and of the volatile matter evolved, causing the oil to harden sooner than does linseed oil without pigment. The presence of white lead tended to reduce the initial oxidation by influencing the diffusion of oxygen. During the later stages of the oxidation the pigment acts as a drier to increase the amount of oxygen absorbed by the oil. The effect of barium sulphate is to retard the oxidation in the initial stages, to decrease the amount of oxygen taken up, and to increase the amount of volatile material which was more than half the weight of the original oil film, which is an extraordinary result !

The behaviour of zinc white is peculiar. In some cases it acts as an inert pigment like silica, in other cases it behaves like lithopone, causing the oil to harden at an early stage in the oxidation and to

reduce the amount of oxygen absorbed and the amount of vapours evolved.

The same authors¹² have examined the action of iron oxide reds (including Tuscan and Venetian reds) on the oxidation of linseed oil containing lead driers. The pigment first inhibits and then accelerates the oxidation of the oil. The iron oxide reds, containing partially hydrated ferric oxide, are more active in accelerating the oxidation of the oil than are the more nearly anhydrous oxides, and the presence of calcium carbonate, by its neutralising action, retards oxidation. Black oxide of iron tends to inhibit initial oxidation of the oil and does not form iron driers. It must be pointed out that the partially hydrated oxides of iron had a higher manganese content, and the results appear to warrant further enquiry.

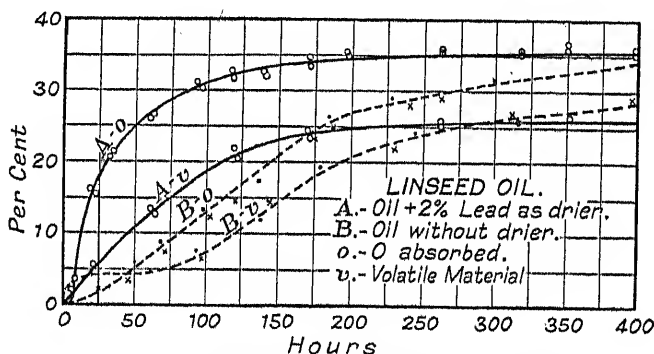
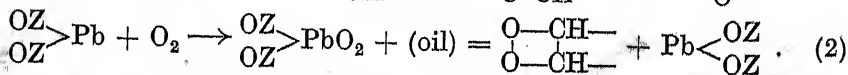
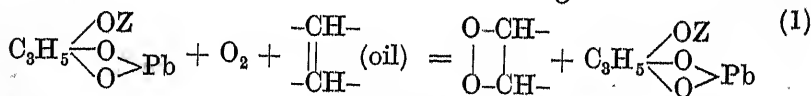
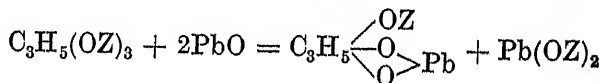
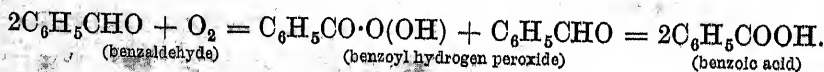


FIG. 7.—Rate of Absorption of Oxygen by Linseed Oil (Rhodes and van Wirt).

The catalytic action of the metallic driers is expressed by Ingle¹³ thus :—



This scheme involves the assumption of the formation of an intermediate substance. The following equations represent the formation and decomposition of similar intermediate peroxide compounds :—



The difficulties in a satisfactory representation of the drying of an oil begin at this stage. What is the fate of the peroxide? Is it polymerised as such, or does it act with more oil according to the following scheme:—



Is the lower oxide polymerised or coagulated to give the solid film? Is the oxide broken down to give aldehyde products which are polymerisable? Summarising the researches on the oxidation of linseed oil, it may be concluded that the initially formed peroxide is not a permanent substance, but gives rise to a variety of products: (1) monoxides of the type AO, which either polymerise, as indicated by H. Wolff, G. Borries and one of the authors;¹⁴ (2) decomposition products of the monoxide, *e.g.*, aldehydes, aldehyde acid and carbon dioxide with polymerisation of the aldehyde components.¹⁵ It is highly desirable to reduce the decomposition products as much as possible, either by preliminary thickening of the oil by heat, or by blending with another drying oil. S. Coffey¹⁵ has shown that, in the oxidation of linolenic acid, 9 atoms of oxygen are absorbed for each molecule of the acid, and that three atoms are liberated in the form of volatile products, whereas linolic acid gives no volatile oxidation products.¹⁶

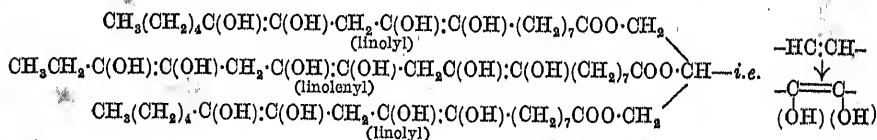
Eibner (*loc. cit.*) has shown that clupanodonic acid undergoes no loss in weight when the solid film has been formed, whereas linolenic and oleic acids show a decided reduction in weight on exposure to the air. Moreover, the peroxide formation and transformation, in the case of the clupanodonic acid, must have been complete, as the iodine value of the film, after 24 hours, had sunk to nothing and there was no "sweating up," but the film was easily attacked by water. In the case of a linseed oil film, the iodine value had fallen to 30.8, whereas a film of poppy-seed oil, after 40 days' exposure, had dropped from 133.4 to 75.5. These figures show the comparative rates of oxidation and transformation in the film even after the oil has set solid, and they are also evidence of the slow passage of oxygen or oxidised products from the surface of the film to the interior. No discussion of the oxidation product of linseed oil can be complete without mention of the pioneer work of Mulder.¹⁷ He exposed linseed oil to ordinary weather conditions from 3 to 10 days, removed the dried films by moistening with ether, and after washing with the same solvent, followed by alcohol and ether, the residue was dried over sulphuric acid and analysed. The following figures are an average for the percentages of carbon, hydrogen and

oxygen: C, 62.47; H, 8.96; O, 28.54; calculated for $C_{57}H_{96}O_{20}$: C, 62.14; H, 8.79; O, 29.07.

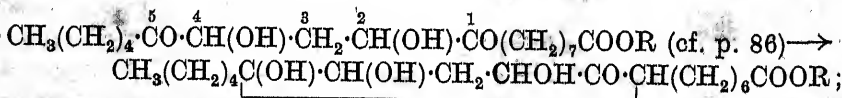
It must be remembered that the analysed product could have no claim for purity, owing to the presence of olein and saturated fats; moreover, the decomposition products previously referred to in the oxidation of linseed oil would give rise to substances not necessarily soluble in alcohol and ether. Mulder isolated a white linoxyn acid which by heating or by action of alkalis passed into a red linoxyn acid.

Recently G. W. Ellis¹⁸ has confirmed Mulder's figures from an exhaustive investigation of the oxidised film. He found that by dissolving the film, previously digested with dry petroleum ether, in a mixture of 90 per cent. CCl_4 and 10 per cent. dry alcohol and after reprecipitating by petroleum ether, dissolving and reprecipitating, a residue was obtained which was soluble in alcohol, and on evaporation gave a residue with the following percentage composition: C, 62.03; H, 9.07; O, 28.90. Ellis states that the formula corresponds to a mixed glyceride of 2 mols. of linolic and 1 mol. of linolenic acids, and that the substance comprised the greater part of the film and was not a mixture. The proposed composition is not in keeping with the results obtained by Eibner from the direct analysis of the oil. Prolonged oxidation of the linoxyn produced a yellowish, thick oil after absorption of 15.7 per cent. of oxygen and the evolution of 9.4 per cent. of carbon dioxide. This result is comparable with the so-called superoxidised oil of Reid. The investigation seems to have been very exhaustive, but in the opinion of one of the authors the conclusions drawn require more experimental support.

Nevertheless Ellis puts forward a new representation of the oxidation which may be demonstrated by the following formula:—

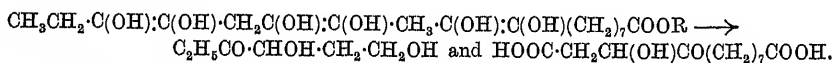


The linolic residues may give rise to hydroxyketones, which may produce closed ring substances:—



whereas the enol form is more persistent in the linolenic residue,

and subsequent change would be accompanied on hydrolysis by a rupture of the chain with a possible formation of substances of the following type :—



The scheme is worthy of further investigation, and the aspect of enolic formation in linoxyn may receive support in the sensitiveness of paint films to traces of alkali, in contrast with the action of paint solvents such as acetone, which is more active in the removal of less completely oxidised oil films.

The exact nature of the oxidised linseed oil film must be left in uncertainty. It is admitted that the peroxide stage is temporary. Whether the peroxide substance passes to a stable oxide or to an enolic compound of the type proposed by Ellis cannot be decided until a systematic investigation of the products of oxidation has been undertaken. This investigation must include the identification of the products of the change. The results of the investigations with ozone as oxidiser are probably not strictly applicable to oxidation under atmospheric conditions. K. H. Bauer and G. Kutscher¹⁹ have investigated the action of hydrogen peroxide and benzoyl peroxide on linolenic and oleic acids, and have obtained markedly different oxidation products, yellow oily acids with strong peroxide reaction and red oily acids with no peroxide reaction.

The accelerating influence of metallic oxides, such as lead, cobalt, and manganese and their salts, is a matter of great practical importance, not only in the production of the solid surface film, but also in its final behaviour. The induction period of oxidation disappears in their presence, and there are differences in the percentages of oxygen absorbed by linseed oil with lead, manganese and cobalt driers. The oxidation curves do not run parallel to that for linseed oil alone, but deviate considerably from the logarithmic curve proposed by Fokin. The term "drying of an oil," or its power to form an elastic film on exposure, is connected with the presence of the glyceryl grouping, and drying appears to be absent when glyceryl is replaced by the ethyl group. The induction period may be connected with an irregularity in the rate of diffusion of the autocatalyst. It must not be forgotten that the important property of a drying oil is that of setting to a solid film on oxidation. The influence of temperature on the drying of oils is that for a rise of ten degrees there is a reduction by a half in the time of drying.

The function of the metallic driers has been illustrated by the equations given in the case of lead oxide with the evidence of the

formation of intermediate compounds. It would appear that the real catalyst is an oxidation product of the oil itself, and the accelerating effect of the driers is due to their action as pseudo-catalysts, promoting the formation of the autocatalyst and thus increasing the rate of oxidation when the oil is first exposed to the air. It must be noted that carbon dioxide is evolved from linseed oil whether driers are present or not, but no hydrogen peroxide is formed when driers are employed.²⁰

The forms in which the metallic driers may be employed are : (a) in a finely-divided state (Livache used finely-divided lead); (b) as oxides (*e.g.*, lead, manganese and iron in umber); (c) as acetates (*e.g.*, lead, cobalt and manganese); (d) as borates (lead, manganese and cobalt); (e) as metallic salts of the drying oil acids (linolenates and linolates, tungates and oleates of lead, manganese and cobalt); (f) as resinates of lead, manganese and cobalt. The oleates are not so soluble nor as active as the linolenates and linolates. There is a tendency to prefer the salts of the highly unsaturated fatty acids, because they are more soluble in oil, paint and varnish thinners. The solubilities of lead and manganese linoleates in linseed oil as determined by one of the writers are :—

Pb and Mn linoleate (22.3% PbO and 5.5% MnO).

In 100 parts of linseed oil after 5 hrs. @ 320° F. : 2.027 PbO and 0.526 MnO.
 In 100 parts of turpentine after 5 hrs. @ 150° F. : 1.67 PbO and 0.6 MnO.
 In 100 parts of linseed oil after 14 days @ 60° F. : 0.4 PbO and 0.095 MnO.
 In 100 parts of turpentine after 14 days @ 60° F. : 2.0 PbO and 0.6 MnO.

Lead linoleate (25.14% PbO).

In 100 parts of linseed oil after 14 days @ 60° F. : 0.5 PbO.
 In 100 parts of turpentine after 14 days @ 60° F. : 4.2 PbO.

It is evident that lead and manganese linoleates are more soluble in turpentine than in linseed oil.

Generally the form in which the metal is introduced into the paint or varnish excludes many common salts of the so-called drying metals, *e.g.*, the nitrates and chlorides are rarely used, whilst acetates and borates are preferred, *e.g.*, borate of manganese, which is colourless, but requires rather a high temperature to yield its maximum effect. Lead tetraethyl, $\text{Pb}(\text{C}_2\text{H}_5)_4$, which is a colourless liquid containing 70 per cent. of lead and freely soluble in linseed oil, is stated to be useless as a drier at the ordinary temperature.

E. Perry²¹ states that an American gallon (7.77 lb.) of linseed oil will take up the following amount of drying substances at tem-

peratures from 270° to 320° F. in the production of fully saturated linoleates, which are solid or semi-solid compounds :—

	Lb.
Lead oxide (litharge)	3.09
Red lead	3.17
Lead borate	4.31
Manganese dioxide (black oxide)	1.21
Manganese borate	2.70
Lead rosinate, precipitated	11.46
Manganese rosinate, precipitated.....	9.61

The above quantities are maximum, and no more of any one of the drying salts can be incorporated with the linseed oil. Linoleates (linolenates, linolates and oleates) dissolve readily in oil at temperatures from 270° to 320° F. (132—160° C.), the latter figure being considered the maximum temperature for solution. After solution any temperature up to 600° F. (315° C.) is permissible, but high temperatures darken the oil in the presence of these driers, as is the case with litharge. Linoleates should not leave any residue, except a small amount of dirt, from the metallic salts used in making them. When linoleates are to be incorporated with tung oil, the raw oil should be heated to 350° F. (177° C.) or 360° F. (182° C.) before adding the linoleates; otherwise if lower temperatures be used, the wood oil separates into two portions, of an equal consistency, when the driers are added and dissolved. Linoleates are used in wood oil for elasticity; in linseed oil, however, they facilitate hardening.

It is impossible within the limits of this book to go into the details of the manufacture of metallic driers. Reference may be made to "Varnishes and their Components" (p. 38), and a pamphlet by H. A. Gardner and R. E. Colman²² (see Appendix to this chapter). Cobalt, manganese and lead are the most popular metals used; other metals, *e.g.*, cerium, vanadium and uranium, have been recommended, the former resembling lead in its action and having approximately the same activity. Vanadium,²³ used in the form of resinate, is stated to be a better drier than manganese, but is inferior to cobalt resinate. In reference to the activity of the metals referred to, the most recent comparisons are given by Ingalls.²⁴

The temperatures at which the driers are incorporated in the oils are worthy of mention. Manganese dioxide (natural and artificial) may be dissolved in linseed oil at 500° F. (260° C.), and not more than $\frac{1}{4}$ lb. per cwt. of oil is used. It is probably taken up into the oil as linoleate, but the boiled oil produced is dark in colour (linoleate is a term used to include a mixture of linoleate, linolate and oleate obtainable from linseed oil). Manganese resinate

(fused, 4.6 per cent.), linoleate (precipitated, 8.9 per cent. Mn), and tungate (precipitated, 9.3 per cent. Mn) are soluble in turpentine and in white spirit. It must be admitted that these salts are more soluble if they are dissolved in a medium as soon as possible after preparation, because their solubility decreases on keeping, due to oxidation giving rise to less soluble products.

Cobalt driers are used in the form of acetate, resinates, linoleate (9.5 per cent. Co), or tungate, and the driers are prepared in the same way as the corresponding manganese compounds. The solutions are as highly coloured as those of manganese, but they do not darken a mixing to the same degree, as the quantity of the metal used is small, and the cobalt-treated oil will bleach out on drying. Lead driers are used in the form of oxide (flake, massicot) or as red lead, preferably as flake litharge. Lead may be introduced into an oil by heating to a temperature of 300—500° F. (149—260° C.), but the oils are dark in colour. It may also be used in the form of acetate in conjunction with rosin to give a resinates (25.6 per cent. Pb). It is preferable to use the oxide dissolved in the oil rather than in the form of the separately prepared linoleate (25 per cent. Pb), because of difficulty in drying the viscous salt.

Manganese resinate, fused	4.6 per cent. Mn
" linoleate, precipitated	8.9 " " "
" tungate, precipitated	9.3 " " "
Lead linoleate, precipitated	27.0 " " Pb
" " fused	27.0 " " "
" resinate, precipitated	25.6 " " "
" tungate, fused	27.1 " " "
" " precipitated	28.0 " " "
Cobalt resinate, fused	3.0 " " Co
" linoleate, fused	5.0 " " "
" " precipitated	9.5 " " "

Other comparisons have been given by Fokin and Eibner²⁵ and by Mackey and Ingle.²⁶ In all the proposed arrangements cobalt and manganese head the list, but in the case of other metals the positions are uncertain and vary with the method employed.

Ingalls' linseed oil films (0.001—0.003 in. thick) containing 2 per cent. of resinates of the following metals:—

	Mn.	Pb.	Zn.	Ca.	Cu.	Fe.	Al.	Cr.	Linseed oil alone.
Drying time (hours) ...	12	26	30	32	46	60	85	95	121
Percentage increase in weight after 12 hours	17.4	9.4	6.5	6.0	4.9	4.1	2.8	2.0	0.93

Fokin : Co, Mn, Cr, Ni, Fe, Pt, Pd, Pb, Ca, Be, Hg, U, Cu, Zn.

Eibner and Pallauf : Co, Mn, (Ce), Pb, Fe, Cu, Ni, (Va), Cr, Ca, Al, Cd, Zn, Sn.

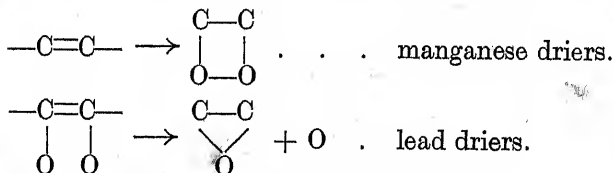
Mackey and Ingle : Co, Mn, Ce, Pb, Cr, Fe, U, Na, Ag, Zn, Hg, Al.

It would appear that a metal which can form more than one oxide acts as a drier or oxygen carrier when it is in an oil-soluble form, provided that the salts of the lower oxides are more stable than those of the higher oxides. It has been stated that the more oxides a metal can form the greater will be its catalytic activity, but according to Gardner²⁷ this statement must be qualified owing to the behaviour of aluminium compounds as driers. Although slow in initial effect, these compounds seem to have a greater drying power than the corresponding compounds of lead. Further investigations with aluminium salts as driers are advisable, although the drying power of aluminium resinate must be admitted.

The method of testing the drying power varies considerably. Mackey and Ingle (*loc. cit.*) employed the following method: cotton wool, soaked in linseed oil containing the metals to be classified, was placed in a cloth-oil tester,²⁸ and the time taken to attain a temperature of 200° was observed. In the case of cobalt that temperature was obtained in the shortest time. Such a method gives a comparison of the intensity of oxidation of the linseed oil in the presence of driers. Ingalls gives the times of drying when the films are dry to the touch. A recent proposition is to determine the time up to the point at which a standard sand ceases to stick to the film. When the stage of surface dryness is reached, fine sand (mesh 30—60) may be easily brushed off the surface, by means of a camel-hair brush, without any sand adhering to the surface.

Much has been written on the specific action of the metallic driers. Manganese and cobalt are looked upon as producing superficial oxidation, whereas lead driers, although much slower in their action, favour the production of a more uniformly oxidised film.

Rochs²⁸ seeks to explain the differences on chemical grounds.



Cobalt driers (oleate or resinate) cause a greater degree of "skin-ning" of stored varnishes than lead or manganese driers. In varnishes containing relatively large percentages of China wood oil, little tendency to formation of skin was observed when a manganese drier was used, whereas thick skin rapidly formed in the case of similar varnishes containing cobalt driers. The minimum of skin-

ning in oil varnishes is obtained by adding the greater part of the drier as metallic oxide to the hardened resin and oil combination, a subsequent addition being made of liquid drier (with exclusion of cobalt whenever possible). (Cf. so-called "drumming" process in varnish making.²⁹) Reference has been made to the peculiar retardation of the setting of varnishes containing cerium (p. 97). The importance of these differences between metallic driers has led to the adoption of mixtures.

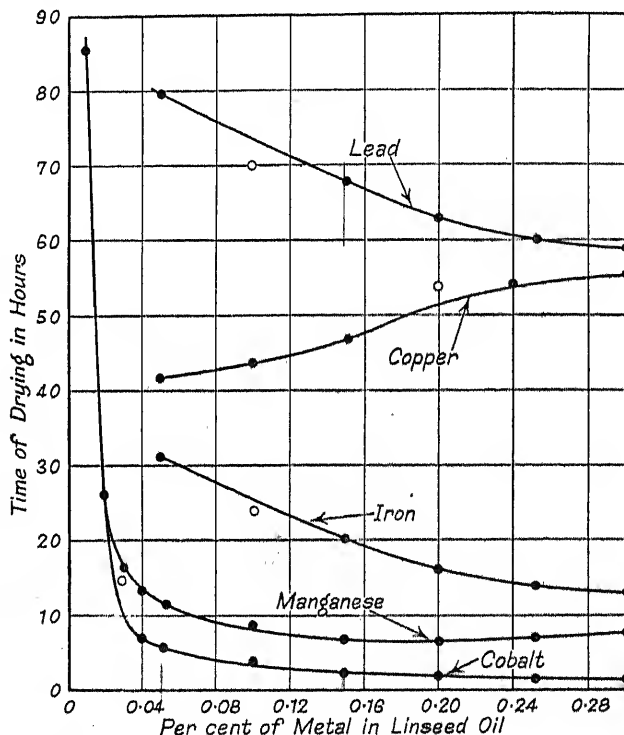


FIG. 8.—Effects of Different Percentages of Lead, Copper, Iron, Manganese and Cobalt on the Drying of Linseed Oil.

Combinations of Driers.—The metallic content of boiled oil and varnishes has no relation to the reacting mass of the oxidisable components owing to catalytic action. According to Weger³⁰ the drying power of manganese increases up to a concentration of 0.2 per cent., but further increase causes no acceleration of drying. He recommends 0.5 per cent. of lead and 0.1 per cent. of manganese as the optimum amount. Meister³¹ states that 0.12 per cent. Mn, 0.45 per cent. Pb, is the best combination, when the metals are present in the form of resins. W. Flatt³² found that the drying

power of lead in linseed oil was at a maximum when 1.9 per cent. of lead was present. Even a combination of manganese and cobalt is sometimes preferable to either metal separately.

In the most recent contribution on the relative catalytic effects of metals on the drying of raw linseed oil, lead, manganese and cobalt, together with iron and copper, were introduced in the form of resinates into linseed oil.³³ The times of drying of the oil with

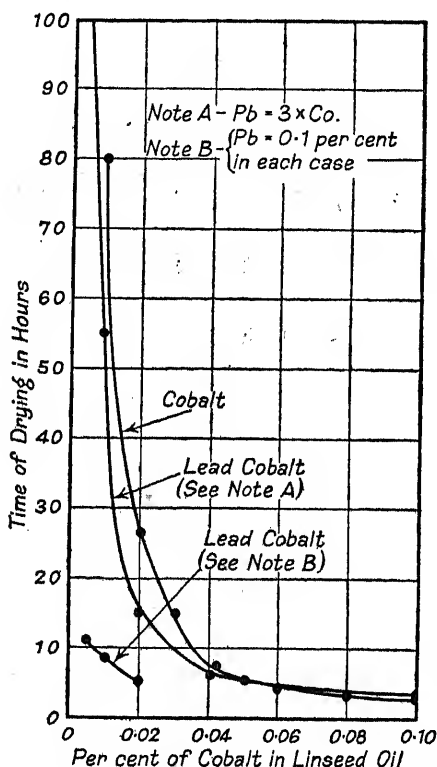


FIG. 9.—Effect of Lead on the Drying of Linseed Oil containing Cobalt.

varying proportions of the metals were determined using the craftsman's test of touch to decide the drying point. The resinsates employed were prepared according to the methods given in Circ. 120; Seeligmann and Ziecke, "Handbuch der Lac- und Firnis-industrie," p. 701, and were incorporated in the oil at 150°. The linseed oil samples, containing definite percentages of metals, were flowed on glass. The excess oil was drained off, and the oil allowed to dry under known temperature and humidity conditions, which conditions may be considered to be normal. Fig. 8 shows the

effects of different percentages of lead, copper, iron, manganese and cobalt on the drying of linseed oil. It appears that neither copper nor lead resinate alone is an efficient drier for raw linseed oil. Iron seems to approach manganese and cobalt in effectiveness when used in comparatively high concentrations. From the experience of one of the authors the presence of iron soaps retards the setting time of a varnish film containing lead and manganese. Cobalt appears to be

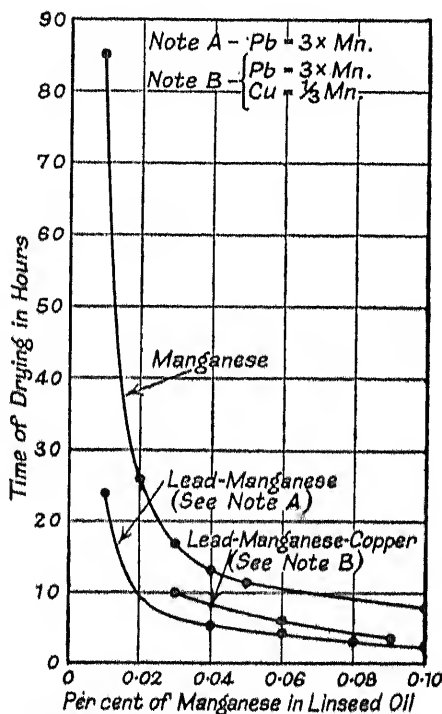


FIG. 10.—Effect of Lead on the Drying of Linseed Oil containing Manganese, and the Effect of Small Amounts of Copper on Samples of Linseed Oil containing Lead and Manganese.

more effective than manganese in concentrations ranging from 3 per cent. to 0.03 per cent.; below this concentration these metals seem to be nearly equal in their catalytic action, which begins to diminish rapidly at this point with further decrease in concentration. There is no advantage in using more than 0.05 per cent. of either manganese or cobalt to cause linseed oil to dry. At a concentration of 0.05 per cent. of metal, taking cobalt as 100, the relative catalytic effects of the other metals studied would be: manganese 46, iron 17, copper 13, and lead 6.5. In Fig. 9 it is seen that if lead be added to linseed oil containing cobalt in the proportion of 3 parts of lead to 1 part

of cobalt, there is very little added catalytic effect when the concentration of the cobalt is above 0.02 per cent. Lead in the same proportion seems to add effectiveness when cobalt is present in concentrations approximating to 0.02 per cent. A greater concentration of lead adds catalytic effect in a marked degree to small concentrations of cobalt. With 0.1 per cent. of lead present an amount of cobalt as small as 0.05 per cent. causes linseed oil to dry in less than 12 hours. If lead be added to samples of linseed oil

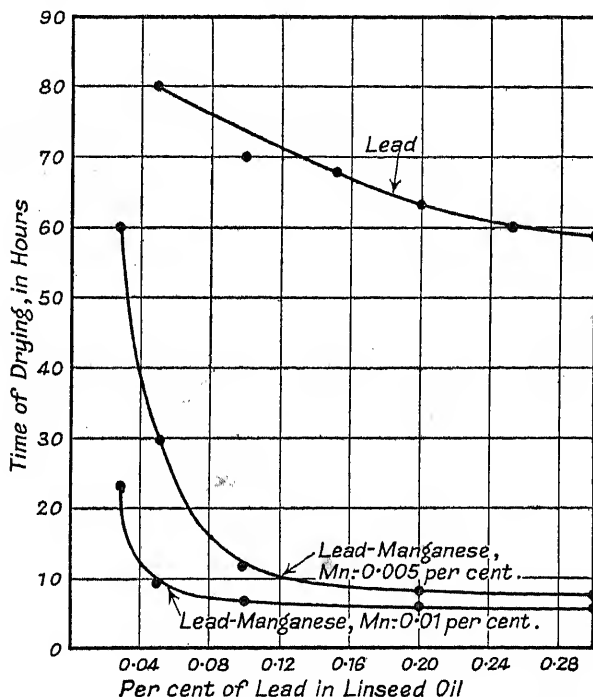


FIG. 11.—Effect of a Constant Small Percentage of Manganese on the Drying of Linseed Oil containing Different Amounts of Lead.

containing manganese in the proportion of 3 parts of lead to 1 part of manganese, there is a marked increase in the catalytic drying effect. A sample of linseed oil containing 0.01 per cent. of manganese is changed in drying time from 85 to 24 hours by addition of 0.03 per cent. of lead (Fig. 10). The addition of small amounts of copper to an oil containing lead and manganese appears to have no appreciable effect upon the drying time, so that the possible introduction of copper into linseed oil from a copper pot has no effect on the drying time. In Fig. 11 it is seen that lead (0.05 per cent.), in combination with 0.01 per cent. of manganese, or more

than 0.1 per cent. of lead in combination with 0.005 per cent. of manganese, represents the most advantageous combination. The details of the above communication are of interest, and many of the statements made are confirmatory of the results of experience in works. The effect of heat treatment during incorporation of the different metals, in the manufacture of a true boiled linseed oil, has not been considered (cf. boiled oils, p. 147).

The advantages of the use of lead are not so marked when dealing with oils polymerised by heat. Reference has been made to a difference in the action of manganese and lead. Experience has shown that the activity of lead driers is less sensitive to temperature variations, whereas manganese driers are peculiarly sensitive.³²

	Drying time at 10°.	Drying time at 5°.
1 part Pb in 100 parts oil varnish	20 hrs.	24 hrs.
1 part Mn in 400 parts oil varnish	20 „	36 „
1 part Mn in 1200 parts oil varnish	10 „	44 „

There is always an increase in the viscosity of lead drying oils on keeping, whilst manganese and cobalt oils change only very slightly; nevertheless a manganese drying oil improves with age. The process of the drying of oil is not entirely determined by the rate of oxidation as influenced by the catalyst. Of practical importance is the hardening and gelation of the oxidised oil, and the uniformity of the setting must be considered. Diffusion of the oxidation through the film must be facilitated, and such diffusion may be represented chemically by the production of a monoxide. The superficial nature of the changes must not be neglected, and the presence of metallic soaps in the film affects the surface tension. The surface of the drying oil is a zone in which various possible intermediate compounds and final products are capable of existence side by side, and in which the actual equilibrium state is such that there is a definite proportion between these possible intermediate products in a kinetic sense; but while the actual number of molecules remains constant, the individuality of these molecules will be continually changing. It is possible to understand how manganese and cobalt can help the absorption of oxygen by linseed oil, by reason of the fact that, among the various possible compounds formed on the surface of separation, there would be peroxides, in which oxygen is at a potential sufficient to be transferred to the oil. It is evident that

the chemical proportion of driers will not fully account for their behaviour.

A comparison may be made between the intermediate compound theory and a physical absorption theory, in which the solid catalyst becomes coated with a single layer of molecules by adsorption, such condensation being accompanied by a change in the character of the adsorbed molecules, involving a dissociation of elementary molecules (*e.g.*, oxygen into atoms) by which the atoms of the condensed molecule are definitely associated with certain molecules in the surface layer, the function of the catalyst being to bring about condensation of the oxygen. The theories of the adsorption school of physicists and the intermediate compound group of organic chemists are on convergent lines.

P. Slansky³⁴ considers that basic catalysts, *e.g.*, lead oxide, act by drawing the glyceride end of the surface molecule inwards and allowing the unsaturated carbon chains to move outwards and become oxidised, whereas substances like carbon black are absorbed at the unsaturated carbon chains which are directed inwards with consequent retardation of oxidation. Such an aspect on the lines of Langmuir and Adam's researches is plausible, but not very helpful unless confirmed by experiments with Langmuir and Adam's films.

(To the industrial chemist the production of a solid oxidation gel is of greater importance than the rate of absorption of oxygen by the drying oil. Starting from the assumption that the oxidation product undergoes further change, to produce a solid substance, it is advisable to review the influence of small quantities of substances which will bring about the desired result. Reference has already been made to the peculiar action of metallic driers such as lead and cerium as compared with manganese and cobalt. Mulder states that lead gives films "tough like rubber," while manganese produces films "tough like leather," although lead is a slower drier than manganese. Recently it has been found that small quantities of solid substances, which can have little or no chemical effect on the properties of the film, nevertheless exert a strong influence on the setting of the oils, even in the presence of metallic driers. The following graph (Fig. 12) shows the effect of small quantities of *o*-amidobenzoic acid on the apparent oxygen absorption of linseed and China wood oils. Although the form of the oxidation curve is in keeping with an autocatalytic reaction (Ostwald) which can be expressed by the equation:—

$$\frac{dx}{dt} = k(m + x)(a - x)$$

a = total volume of oxygen absorbed; x = volume of oxygen absorbed in t days; m = a constant, proportional to the concentration of the catalyst.

If m be negligible, then :—

$$dx/dt = kx(a - x)^{.35}$$

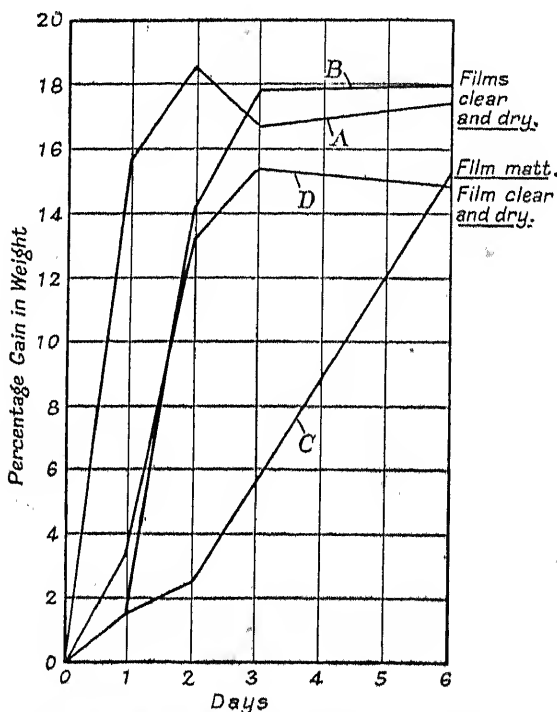


FIG. 12.—Influence of *o*-Amidobenzoic Acid on the Oxidation and Setting of Linseed and China Wood Oils.

A = Linseed Oil + 0.01% Mn + 1% *o*-amidobenzoic acid.

B = " " " " " " " " " " " "

C = China Wood Oil + 0.01% Mn.

D = " " " " " " " " " " " " + 1% *o*-amidobenzoic acid.

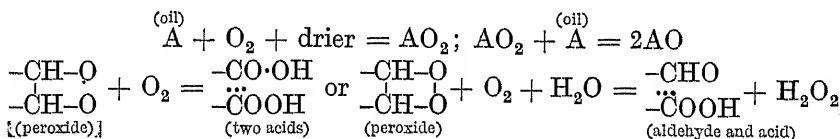
The empirical formula of Orloff cannot be accepted as representing the change during the oxidation of linseed oil.

$$k = \frac{1}{t(A + B)} \log_e \left(\frac{A}{A - x} \cdot \frac{B + x}{B} \right)$$

k = velocity constant; A = total apparent oxygen absorption; B = constant. The reaction is heterogeneous, and so many substances are involved that the equation cannot be reliable.

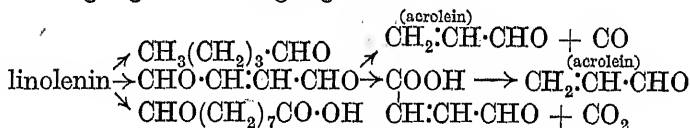
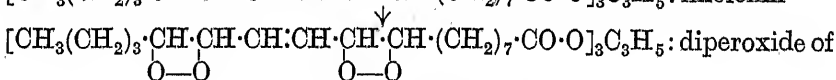
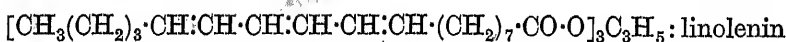
Viewing the oxidation of linseed oil from a chemical standpoint,

it may be concluded that peroxides are the initial products of oxidation. It seems probable that these peroxides part with their oxygen gradually to form oxides. The nature of the oil and the conditions of oxidation will decide whether these peroxides undergo destructive decomposition with the formation of degradation products (acidic and volatile), or whether monoxides produced according to the following scheme:—



polymerise or coagulate. This is the most important consideration in connection with the value of a drying oil.

Salway³⁶ suggests that linoxyn consists of olein and polymerised aldehydes, derived from the decomposition of oxidised linolin and linolenin, glycerides of linolic and linolenic acids respectively. He assumes for linolenic acid the constitutional formula of a derivative of hexatriene, in order to account for the presence of acrolein and oxides of carbon among the volatile oxidation products of the oil:—



The constitutional formula of linolenin rests on the work of Raspe and Erdmann, and Salway's suggestion requires rearrangement of the double linkages during the process of oxidation. From a chemical standpoint the oxide formation, with polymerisation or coagulation proceeding simultaneously with the decomposition of the peroxide into simpler substances of an acidic character, seems more in keeping with facts³⁷ (see p. 93).

The influence of small quantities of solid substances on the setting of oil and varnish films, without reduction in the rate of absorption of oxygen is shown in the accompanying graph (Fig. 13). Salicylic acid has a softening action on the "oxyn," either of linseed oil or China wood oil; *o*-amidobenzoic acid has also a softening action. The presence of these substances actually accelerates the rate of absorption of the oxygen, and the time of setting is reduced

especially in the case of tung oil, where the hardening is very slow indeed. It is evident that a freer diffusion of the oil in the film has been brought about by the presence of these catalysts. Linoxyn may be considered as a lattice-work system, in which a semi-solid film encloses a liquid phase containing unoxidised oil. In some forms of linoxyn the enclosure of unoxidised oil causes the film to

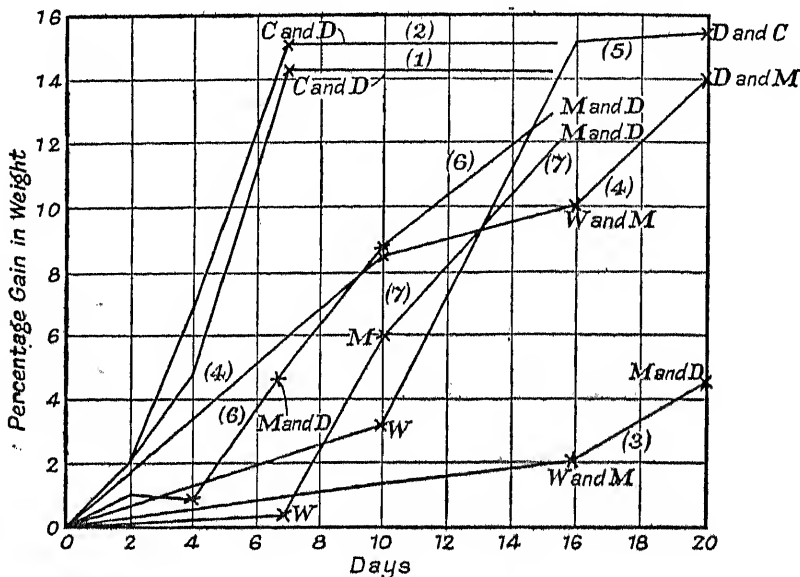


FIG. 13.—Influence of Salicylic Acid on the Oxidation and Setting of Linseed and Tung Oils.

- (1) Linseed oil + 0.01% Mn.
- (2) " " " " + 0.5% Salicylic acid.
- (3) Tung oil " " " " + 0.5% " "
- (4) " " " " + 0.5% " "
- (5) Linseed oil " " " " + 0.5% " "
- (6) Tung oil " " " " + 0.5% " "
- (7) Tung oil " " " " + 0.5% " "

Temp. 40—60° F. in a current of filtered air.

Films (1), (2), (6) and (7) : 0.05—0.06 gm. in weight.

Films (3), (4) and (5) : 0.1—0.13 gm. in weight.

C = clear; D = dry; M = matt; W = wet.

have undesirable properties. It is to be expected that driers such as cobalt and manganese would act differently from lead in giving a more heterogeneous gel. It is possible that the difference between the surface tensions of lead, manganese and cobalt soaps affects the nature of the coagulated film. The surface activities of a rosin ester-wood-oil film, containing manganese driers is very marked, compared with the comparatively neutral surface of a linseed oil varnish containing lead. Dr. Norrish using his ethylene and bromine

method has found that the rosin-wood-oil varnish films are strongly polar, double that of the lead copal varnishes.

The surface tensions of the films of the above varnishes towards water, as indicated by measurements of the contact angles determined by N. K. Adam, is evidence in favour of the surface activity of the China wood oil film containing no lead. The condensation of moisture on such active surfaces is the precursor of the well-known defect of "bloom." It is surprising that the non-blooming films have a greater water-absorbing power than surfaces prone to bloom. The condensation may be due to the sweating up or syneresis of the imprisoned unoxidised oil in the gel, which, on oxidation in a dust-laden moist air, produces a deposit of moisture caused by an electronic effect. It is noticeable that the presence of dust accelerates the condensation and the moisture-laden dust, acting like a sponge, brings about a rapid "veiling" of the surface.

APPENDIX

The details of the preparation of several typical metallic driers, selected from Gardner and Coleman's pamphlet (*loc. cit.*), are of interest, and methods of manufacture of precipitated manganese linoleate, fused cobalt linoleate and fused manganese resinate may be selected.

Preparation of Precipitating Manganese Linoleate.—Saponify 100 lb. of linseed oil in a steam-jacketed kettle of 100 gallons capacity with 114 lb. of caustic soda (18° Bé.) according to the directions given in the pamphlet for the saponification of drying oils. Dissolve the manganese salts (chloride or equivalent) in 20 gallons of water. It is essential that in the precipitation of manganese linoleate the solutions should be used at a temperature of about 80° F. The temperature of the manganese solution should be about 70° F. and that of the soap about 100° F. If the solutions be too warm, the precipitate becomes very heavy and clots together in a ball. When the solutions are cold, the manganese linoleate precipitates out as a flocculent precipitate which soon becomes granular. After the manganese linoleate is precipitated and the solution has been warmed in order to bring the mass together so as to draw off the separated water, care should be taken that the solution does not become so hot as to cause it to mass together to such an extent that the wash water will not separate it again. After the soap is washed it should be pressed and dried, by heating it in linseed oil, at a temperature of 250° F., until all the moisture is driven off. This is indicated when the foaming has stopped and a sample on glass

remains clear when cold. From 3 to 4 lb. of manganese linoleate can be dissolved in 1 gallon of oil. The soap can also be dried by direct fusion, to expel moisture, and then immediately dissolved in turpentine. It must be pointed out that the freshly-precipitated salt must not be left exposed to the air for more than a few hours after precipitation, because the oxidised material is much less soluble in oils, turpentine or white spirit.

Preparation of Fused Cobalt Linoleate.—For 100 lb. of the fatty acids of linseed oil $22\frac{1}{2}$ lb. of cobalt acetate are required for the preparation of a linoleate containing approximately 5 per cent. cobalt. The cobalt acetate should be added at 250° F., allowing time between each addition for the water present in the acetate to be expelled. After the acetate is all added, raise the temperature to 400° F. If the increase in temperature has been slow, the combination will have been effected by the time this temperature is reached. Otherwise keep at 400° F., not above, until a clear violet-red colour is seen. The fused salt is readily soluble in oils, turpentine and mineral spirit.

Preparation of Fused Resinate of Manganese.—A common practice among varnish-makers is to fuse resin with black or recovered oxide of manganese and some drying oil. A material of better quality and stronger drying properties can be made by using precipitated manganese hydrate. The manganese hydrate is prepared by adding an excess of a warm 20 per cent. solution of caustic soda to a warm 25 per cent. solution of manganese chloride, each solution being at 120° F. If cold solutions be used, the precipitate is much finer and harder to filter. After the manganese hydrate is precipitated, it should be well washed, pressed, and finally dried in thin layers in a drying-room. After drying it should be finely ground. Melt 100 lb. of rosin at 350° F. Mix 8 lb. of the precipitated manganese hydrate with 1 gallon of linseed or soyabean oil. When the rosin is melted, slowly add the manganese oil mixture to it so that the foaming is not excessive. When it is all added, raise the temperature to 450° F., and hold the mass at this temperature until it attains a distinct brown colour, becomes clear and shows subsidence of foam. Then raise to 500° F. and cool. The distinct brown colour referred to indicates the end of the cooking period, and represents the point at which the manganese hydrate has completely combined with the rosin. When the manganese is first added to the melted rosin the mass has a muddy brown appearance, which disappears after heating for 40—50 minutes at 450° F.

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CHAPTER IV

EXPRESSION AND EXTRACTION OF LINSEED OIL AND CHINA WOOD OIL

Linseed Oil.

LINSEED oil is obtained from the seeds of the flax plant (*Linum usitatissimum*). The plant is cultivated chiefly for its fibre. The oleaginous seeds are exported from the following countries, Argentina, India, Canada, Russia (the Baltic Provinces), Morocco, China, and are grown to a limited extent in the British Isles. There are two varieties of the seed, the white and the red, the oil produced from white linseed being considered to be of a superior quality.¹

The importance of British-grown linseed is unfortunately not so appreciated as it ought to be; especially considering the quality of the oil. In the pamphlets issued by the British Flax and Hemp Growers' Society, Ltd., Nos. 1—7, Eyre demonstrated that linseed can be grown successfully in England and that the yield of oil is superior to that obtained from foreign varieties. Eyre and Morrell showed that cake made from English-grown linseed is quite equal to that made from foreign seed; whilst the oil obtained is not inferior to the best "Baltic" oil. It is reported that 50—70 gallons of oil per acre were obtained if the seed were solvent-extracted; or 35—45 gallons per acre if the seeds were crushed.

The pamphlets published by the society deserve the attention, not only of the farmers, but also of the seed-crushing industry and of the paint and varnish and linoleum manufacturers.

In the historical survey of the flax industry in England it is stated that in 1535 an Act was passed making the cultivation of flax and hemp obligatory, and thirty years later this law was made more stringent, a fine of five pounds being imposed on all farmers not growing at least 1 acre of flax or hemp for every 60 acres of land cultivated.

In India and Canada fibre and seed crops are grown, but in Argentina no flax fibre variety is grown (*British Empire Review*, March, 1925).

It is interesting to note that in 1870 there were 23,957 acres devoted to growing flax in Great Britain. This amount gradually decreased, and in 1910 there were only 229 acres devoted to flax. During the War, the area was much increased and five flax factories were laid down, and although few of the factories now exist, yet there is a large and increasing area of cultivation of the dwarf or seed variety.

The society recommend that the best seeds to be grown are the

variety known as La Plata or Plate, in preference to the Moroccan or Dutch.² This variety is grown for seed only, and not for fibre.

Both the oil content—an average of 40 per cent.—and the weight of the individual seeds compare most favourably with the average of the best imported from India. The society has proved the opinion to be quite erroneous that the linseed raised in this country is inferior to that which can be imported, and that the oil is less in quantity and lower in value than that which is obtained from foreign seeds.

The high iodine values, and high percentages of hexabromides and low viscosities of the oil from English-grown seed have shown the oil to be not inferior to Baltic oil, and actual practical works experience definitely proves this conclusion.

In an interesting survey of the world's production of flax seed and linseed oil³ (*Commerce Monthly*, New York, June, 1923) it is shown that during the past four or five years Argentina has produced more than half the world's output of linseed.

Approximate World Production of Flax Seed. (In thousands of bushels.)

Country.	(5-year average).		1919.	1920.	1921.	1922.
	1909-13.	1914-18.				
Argentina	31,117	26,921	42,038	50,470	32,272	47,000
British India	19,870	18,401	9,400	16,760	10,801	17,360
U.S.A.	19,505	12,922	7,256	10,774	8,029	12,238
Canada	12,040	6,771	5,473	7,998	4,112	5,009
Russia in Europe	21,336	16,303*	— †	—	—	—
Other countries ...	5,756	7,830	5,041	6,048	6,795	5,283
Total	109,624	89,148	69,208	92,050	62,009	86,890

* Two-year average, 1914-15.

† Not available.

The yield of seed from fourteen producing countries in 1922—23 was 80,260,000 bushels, in 1923—24, 112,563,000 bushels; from twenty-eight countries in 1922—23 the amount was 94 million bushels.⁴

Prior to 1916, Russia was one of the largest producers of flax seed, but since that year Argentina, British India, the United States and Canada have produced 90 per cent. of the total supply. Although the acreage of the Argentine crop in 1922 was 1 per cent. above the pre-war average acreage, yet the crop was estimated to be 50 per cent. greater. In British India, the second largest producer, the average acreage was 20 per cent. less than the pre-war area, whilst

the supply is dependent on weather conditions. In the United States and in Canada the decline is more marked, due partly to the competition of wheat, which is a more profitable crop. Mills for the extraction of oil from flax seed are chiefly in the United States, the United Kingdom, the Netherlands, Germany, France, Belgium and Italy, which are the principal consumers of linseed cake and oil. It is much less expensive to transport the seed than to crush it in the country of origin. The above countries crush more than 95 per cent. of all flax seed entering into national commerce and, because of large imports of seed, some European countries, although not producing seed, are important exporters of linseed oil. Before the War Germany was the largest net importer of flax seed, but in 1922 the supply had dropped to one-third of the pre-war volume. It is estimated that the consumption of linseed oil in Europe in 1922 was probably 40 million gallons less than pre-War, but decreased consumption in Europe is counterbalanced by increased consumption in the United States, which imported 19 million gallons in that year. Steps are being taken in the last-named country to prevent the decline of home production. The maintenance of the immediate demand for linseed oil will depend in a large measure on widespread continuance of the building activity.

Crushing of Linseed.—The expression of linseed has been known and employed from the remote ages, and has now practically resolved itself into the use of two systems: the Plate (Anglo-American) and the Cage systems.

The seed is sold on the basis of at least 95 per cent., which is often 97 per cent. pure; Indian seed is generally the most free from foreign seeds, and contains 37—43 per cent. of oil.

The seed is elevated from the barge to the hopper of the automatic weighing machine, from there to the cleaning machinery, and thence to the silo or storage house to await treatment.

The seed is first passed through a magnetic separator in order to remove all pieces of metal which might cause breakdown or stoppage in the subsequent grinding. It is then delivered by a worm conveyor to the screening machine. The details of the plant used may be found in T. W. Chalmers' "Production and Treatment of Vegetable Oils." As a rule, a good screening machine should treat 28 to 30 cwt. of linseed per hour.

The seed is then conveyed to the feed hopper of Rolls or Crushing machinery, where it is pulverised or, more correctly, rolled. Success in the subsequent expression of the oil is dependent on this crushing process. The rolls must be in perfect trim and accurately

turned, and require constant attention to be kept true for perfect crushing. Reference for description of the rolls may be made to Chalmers' work. After conversion into a meal the seed is elevated into the Kettle or Cooker, where it is heated in order to facilitate the expression of the oil, liberated by the rupture of the oil-containing cells, and to coagulate any albuminous matter present.

The kettles are made of cast iron or from boiler plate, steam-jacketed on the inside and bottom. Wrought-iron stirrers are fixed to a vertical steel shaft. A pressure gauge, safety-valve and a temperature recorder are fitted to the kettle, also a steam inlet valve to the jacket. Open steam is admitted to the kettle to add moisture to the seed, and this open steam must be carefully regulated.

The whole operation of heating and mixing and tempering the crushed meal is most important. The temperature should be very carefully controlled and should not be higher than 180—200° F. Many crushers prefer lower temperatures than these, and thus obtain a paler-coloured oil with a lower acidity. Double kettles are strongly recommended for the treatment of crushed linseed.

The inflow of the dry meal and withdrawal of the cooked meal should form a continuous process, care being taken not to "pack" the kettle with too much meal. The meal is immediately drawn off into the moulding machine of Former, from which the cake, wrapped in the press cloth, passes to the press.

Anglo-American Press.—The press generally takes 16 cakes, about 28 inches by 12 inches. The press-head and base are made of cast iron and the base is fitted with a steel gutter to catch the expressed oil. The hydraulic cylinder is of cast steel, fitted with a ram. The whole press should withstand a working pressure up to 2 tons per square inch on the ram.

The ram plate is of cast iron and the intermediate plates should be of solid rolled and of forged steel. The corrugated press plates, are supported in the press by steel studs, on strong cast-iron racks, the latter having a wrought-iron strengthening bar, which also serves as a guide to the plates. Instead of racks, links can be used to support the press plates.

Where it is desired to have a brand imprinted on the cake, the design is inserted into a space milled in the side of the plates.

The presses are usually arranged in batteries of four or six. When a press is full of moulded cakes, the pressman turns on the hydraulic pressure to the press from the accumulators or pumps. The oil begins to flow as soon as the pressure rises, at first slowly, then more rapidly; usually the cakes are subjected

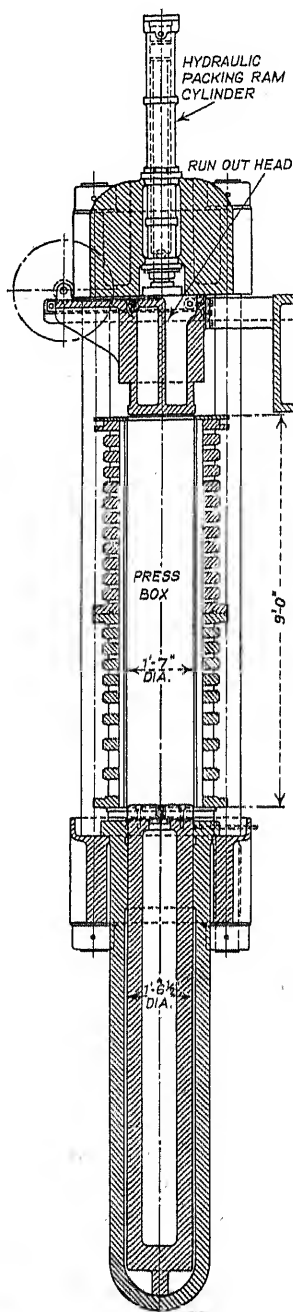


FIG. 14.—Stave Box Press,
"Premier" type.

to a low and then a high pressure. The fixed period in which the presses are allowed to remain under pressure varies from 10 to 40 minutes. For the production of cake to contain a higher percentage of oil, seven or eight pressings per hour are taken from the four presses, but it is not possible to work the open press at higher speeds, owing to excessive "foots" with rich oil seeds. When the pressure has been turned off, the ram descends and the cakes are removed. The cloths are stripped off, and the cakes are placed under a paring machine, which removes the oily edges of the cake, which are ground up in edge-runners and returned to the kettles again. The pared cakes are removed into racks, allowed to cool, and stored in the cake warehouse. The stripping and wear of the press-cloths constitute a serious cost in the crushing.*

Cage or Perforated Box Press.—To reduce the cost of cake-cloths the cage press is used, where woollen or hair cloth is employed. These, however, do not enclose the seed, as do the press-cloths in open presses, and the wear and tear on these mats is not excessive. The cage takes the whole force of the pressure created, the innumerable fine perforations in it allowing the oil to escape, while retaining the solid matter. The extracting boxes are built up of steel staves, which are so made that when placed together they form minute perforations of the box. These perforations should be formed on one side of the staves only, the other side being perfectly flat so that each stave may bear quite solidly on the other, preventing "spewing" of the material from the boxes.

* The press-cloths are woven from fine worsted yarns.

Finally, the whole box is supported on the outside by solid weldless steel rings, which must take all the strain whilst the meal from the seeds is under pressure in the box.

The cake presses are usually operated in blocks of two. The seed is treated the same as for the Anglo-American press, and is delivered from the kettle, in the bottom of which are openings, which correspond to chambers in the press-head. These measuring chambers in the press-heads are just large enough to contain sufficient seed for making one cake in the press, and they are opened and closed at the top and bottom alternately by means of slides.

The workman withdraws, by means of a rack and handwheel, the loose head-block from between the press-head and press-box, and so fills the press.

The ram of the press is pumped up to within 3 inches of the box, the space thus left being sufficient to take the first charge of seed, and the hydraulic liquid in the cylinder is allowed to exhaust gradually.

A press plate and press mats having been placed on the top of the ram, the workman opens the slide from the kettle to the measuring chamber in the press-head, thus allowing a charge of meal to pass into the chamber.

By a reverse movement of the hand lever, the slide at the top of the chamber from the kettle is closed, and the slide at the bottom opened, the measured charge falling into the press-box.

The lever is again reversed to fill the measuring chamber again from the kettle, and the workman levels the charge of seed by hand, then puts a press mat, a press plate and another mat on the top for the next charge of seed.

When the press-box is filled by repeated operation, the loose head-block is returned to its position between the press-head and the press-box, and hydraulic pressure applied. The working pressure may be up to 3 tons per square inch of the ram.

While one press is left under pressure, the other is emptied and recharged.

To empty the press, the hydraulic pressure is released, the loose head-block run out, and the pressure is applied again to force the cake and plate out of the box.

Linseed is not usually crushed in England by the Cage process, but this method is adopted in America, and undoubtedly the process will in the near future be much more used for linseed.

The oil from the presses, either Anglo-American or Cage, is pumped into storage tanks to allow any mealy matter to settle and then filtered,

pressed and pumped into stock tanks, from which it may be filled into the usual barrel or steel drum.

The whole operation in a modern seed-crushing mill is under the supervision of both engineers and chemists.

Samples of the oil as received from the presses are constantly being tested for brightness, colour, free acid and refractive index. The colour and free acid denote whether the meal is being cooked correctly in the kettle. The refractive index is plotted on a chart to give the iodine value, which is a value indication of the quality of the oil. The cakes are tested for the moisture and oil percentages.

For rich oil seeds and for cold pressing the Cage process has decided advantages, but for dealing with a wide range of seeds and producing a high oil yield, the Anglo or open-type press, with its simplicity and low upkeep costs, is by no means supplanted. It is still the utility plant of the mill (J. Brewis ^o). The highest possible yield of oil is not the only consideration in seed crushing; the production of cake that will satisfy the requirements of the farmer must also be taken into account. A cake containing a high percentage of albuminoids and a low percentage of oil, especially linseed oil, is not desirable. The oil content of the most important straight feeding cakes is as follows:—

	Per cent. of oil.
Linseed cake	7 —8
Coconut cake	6½—8
Groundnut cake	7 —8
Palm-kernel cake	6½—8
Cotton-seed cake	5 —6

Oil Extraction by Solvents.

The process of solvent extraction has been recently developed to a considerable degree, and there is every reason to predict that this process will be used to a far greater extent. The gain in the amount of oil obtained is a great advantage—as only 1 per cent. of oil is left in the meal, as against 8—10 per cent. left in the cake from a pressing plant—especially as the oil is generally the most valuable portion of the seed. Unfortunately, the extracted meal is not so popular as a cattle-feeding stuff in England as abroad, and linseed is not solvent-extracted in this country. If a seed meal is to be used for fertilising purposes, it is important that it should be as free as possible from oil, since oil produces “soil sourness” and induces fermentation and spontaneous combustion during storage. Again, a fertiliser containing oil decomposes only very slowly under soil conditions and hence is considerably reduced in value.

Some objections to this process are: the oils are more difficult to refine, as they are darker in colour and they may contain more free fatty acids. The extracted meal containing less oil, lowers its value as a foodstuff. The danger of fire from inflammable solvent is now not so great, particularly when the plant has been constructed upon modern lines. Unfortunately, the less inflammable solvents are more costly and have other disadvantages. If they contain chlorine, this may produce hydrochloric acid, which may attack the works plant, and also have a toxic effect in the meal.

Table of Suitable Solvents.

	B. p.	Specific heat.	Latent heat calor. gr.	Price per gall.	S. G.
Carbon bisulphide	46.2°	0.24	83.8	<i>s. d.</i> 3 7	1.292/2
Chloroform	61.2°	0.23	58.5	25 2	1.50/15
Carbon tetra-chloride	76.7°	0.2	57	6 2	1.63/2
Benzene (comm.)	79/125°	0.408	95	1 3	0.8839/14.2
Light petroleum	90/110°	0.454	73.5	1 6	0.75
Trichloroethylene	88—120°	0.233	57.8	5 3	1.47
Turpentine	159°	0.41	74	4 10	0.8617—0.889/15.5

Messrs. Rose Downs and Thompson (Mr. Bellwood) suggest the following conditions for an ideal solvent:—

- (a) It should neither be inflammable nor explosive.
- (b) It should vaporise with the use of the minimum amount of heat.
- (c) It should dissolve only the oil from the meal of the seeds.
- (d) It should have good solvent properties.
- (e) It should distil within narrow limits of temperature, leaving no non-volatile residue.
- (f) It should have no toxic effect on the health of the work-people.
- (g) It should not cause chemical change in the material under treatment.
- (h) It should have no deteriorating action on the works plant.
- (i) The cost must be low.

As no solvent fulfils all these conditions, the choice must be light

petroleum as against the others. Carbon bisulphide is poisonous, whereas light petroleum is comparatively cheap; light petroleum is colourless, does not injure metal and does not affect the worker, unless he inhales the vapour in large quantities. The best kind of light petroleum should have an initial boiling point of 90° and distil off completely at 110° ; the specific gravity should be about 0.750.

The process of extraction consists in :—

- (1) Proper grinding of the seeds, so that the solvent will readily extract the oil from the meal.
- (2) Allowing the solvent, cold or hot, to percolate through the meal in an enclosed pot or pan.
- (3) Draining off the mixture of solvent and oil from the meal into a still.
- (4) Distilling off the solvent from the oil by heat and condensing some for use again.
- (5) Removing the solvent contained in the meal by heat, and condensing it as a liquid for further use.

The seeds are treated in much the same manner as in the pressing process. They are screened and crushed between the sets of rolls. The condition of the meal from the rolls is most important, as the meal should be more as " flakes " than as a powder. The meal is charged to the extractors, and then sealed up. The solvent, hot or cold, is admitted to cover the meal, the air being allowed to escape by special arrangements. After a short interval of about 20 minutes, varying with the seed, the solvent containing the oil is allowed to drain down and passed to the evaporating tank.

This flooding of solvent on the meal is continued three times or more. The usual process is to use for the first flooding the solvent from the last previous extraction, if the solvent be not fully saturated with the oil.

The solution of oil in the solvent is heated in a tubular evaporator, in which the spirit is distilled off, leaving the oil, which is further heated with steam to remove the last traces of the solvent, and the oil is then pumped into storage tanks.

The meal in the extractors or pots is practically oil free, and is heated with steam at the bottom through a perforated coil, whilst the stirrers are set going to assist in opening out the meal. The steam vaporises the solvent in the meal, and is condensed. The extractor doors are then opened, and the residue removed by the stirrers into a drying machine. The moisture content is kept within

5 to 13 per cent. The meal is slightly crushed to break up any lumps and bagged up by an automatic weighing machine.⁵

The sooner the oil is extracted after ripeness is attained the higher the quality will be, quite apart from the loss that occurs in storage or transit through the inroads of insect life. Most seed-bearing materials are susceptible to fermentation, and many of them contain an enzyme capable of splitting the neutral oil or glyceride, producing rancidity and increasing the difficulties of the refiner. The presence of the natural moisture, which, of course, is greater when the seed is fresh, usually represents a disadvantage, but in the case of the "Scott" process the method of extraction entirely overcomes this difficulty, inasmuch as the process simultaneously dries and extracts (Fig. 15).

The particular feature of the "Scott" plant to be noted in this connection is the small vaporiser at the side of the extractors, which distinguishes the "Scott" system from all others. This vaporiser delivers the solvent vapour just as steam is received from a boiler. This solvent vapour permeates the material, and in doing so eliminates the initial or natural moisture without breaking down the structure of the seed, etc. The vapour, in addition to drying, dissolves out the oil producing a very strong solution. The vaporising process is usually followed by washings of the solvent before it is again employed in the last stages prior to the steaming off.

The above treatment leaves the material in a crisp, dry, hot condition with only a trace of solvent remaining, and it is from this favourably prepared material that the steam is now required to drive off the last traces of taint.

The steam enters a hot apparatus, and comes in contact with a hot material in an open porous form, searching every portion of it quickly and without the opportunity for condensation. The result is not only the complete elimination of the solvent, but a residue is left which contains only from 10 to 14 per cent. of moisture, which for most purposes requires no subsequent treatment, but may be cooled off and bagged immediately. The modern vaporiser attached to the "Scott" plant is horizontal.

The oil and the solvent are now separated by distillation. Realising the deficiencies of the ordinary bulk still for this purpose, where in the final stage it is found extremely difficult to eliminate the last traces of solvent from the oil, Scotts have patented an entirely new process of distillation, carried out in the "Scott" Patent Continuous Still (Fig. 16). In this new still, they have what makes in effect a series of stills superimposed, but the con-

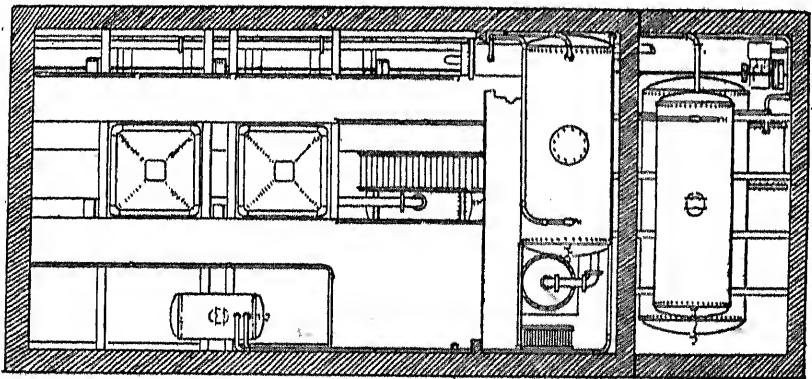
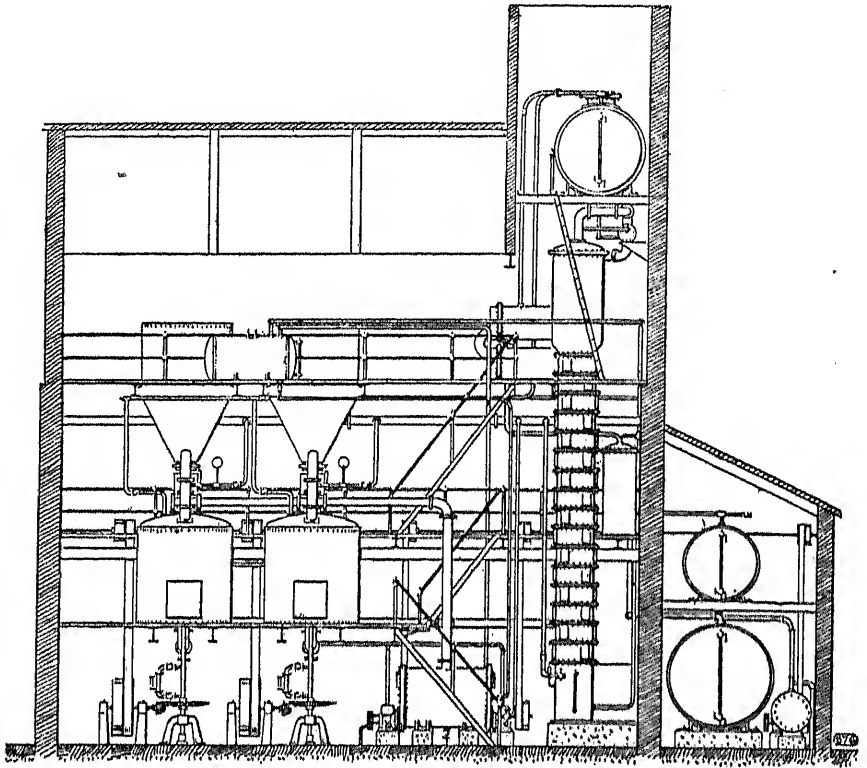


FIG. 15.—Scott Extraction Plant, 16—24 tons Seed per 24 hours.

struction of these stills is somewhat peculiar. Each still or section of the combined column consists of a shallow chamber, in which there rests a thin layer of liquid, *i.e.*, oil and solvent in varying degrees of richness. Projecting through the bottom of the still are a number of uptakes, through which the vapour from the section or still below is allowed to pass. It cannot, however, escape freely, on account of the cap with saw teeth which covers the opening, the teeth being submerged below the surface of the liquid. The gas can, consequently, only escape by bubbling through the liquid in a number of minute bubbles. The liquid is, by a series of baffles, caused to pass in a tortuous direction to and fro before it escapes through the seal into the still below. In this way it is searched progressively and completely by the rising vapour. Each of the stills is similar, except that they are alternately left- and right-handed as regards the inflow and outflow.

The weak mixture is passed through the heater, where it is heated by the escaping vapours into the first section and so passed, subjected to the process

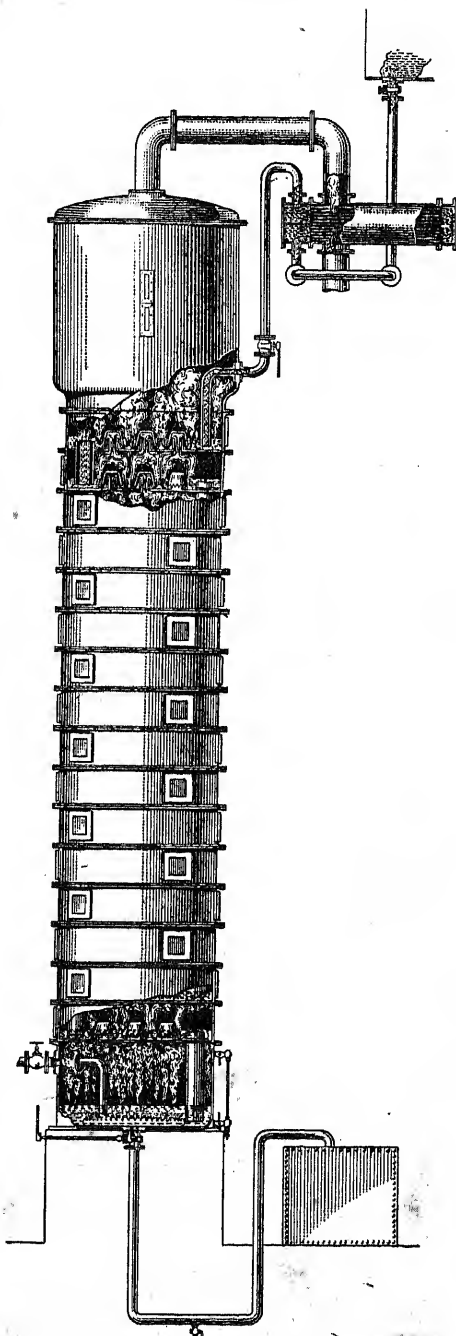


FIG. 16.—“Scott” Patent Continuous Still.

above described, slowly from still to still downwards, until the oil reaches the bottom chamber, where it escapes continually through a seal, free from solvent.

The steam for distillation in this apparatus is used always in the free form, and is admitted only to the bottom chamber. In this way the oil in the bottom chamber contains only a most minute fraction of solvent; as a matter of fact, it is arranged as a precaution that the oil is free from solvent in the chamber above. The whole of the steam required for the distillation is thus caused to pass through the oil, which requires the most searching treatment to remove the last traces of solvent. It then passes through to the section above, where there is slightly more solvent, and in this way it gradually reaches (accumulating as it goes along an accompanying amount of solvent vapour) the top sections of the still, where it has to play on a solvent comparatively weak in oil.

The advantages of the still are that it is continuous in action; it is adjusted at the beginning of the day and continues delivering oil free from solvent so long as it is supplied with steam from the boilers and the mixture from the storage tank; and it is economical in steam consumption, which is about three-fifths only of that required in the older form of still. The oil is definitely freed of any traces of solvent, and is from beginning to end only in contact with the heat for 12 minutes, so that the bad effects resulting from the continued application of heating with wet steam on the quality of the oil, in the matter of colour, flavour, and production of fatty acids, are avoided.

When dealing with nearly all oil-bearing seeds, it is necessary that the extractor should be fitted with stirrer gear. In the "Scott" process the stirrer is used at brief periods only, and is of great assistance in discharging the finished materials through the doors near the bottom. The "Scott" plant is fitted with large vapour pipes, which are essential to liberate freely the attenuated vapours towards the end of the process.

The extraction process requires about 3 cwt. of coal per ton of seed treated, and the loss of solvent is 3 gallons of petroleum spirit (the standard spirit referred to above) per ton of seed. The labour costs vary according to the size of the plant, but in a plant of average size bear an insignificant proportion to the other costs.

In a comprehensive paper on the extraction of oil from seed, nuts and kernels, J. Brewis⁶ has given in some detail the main features of the older crushing process and the more modern solvent extraction one. For many years the pressing or expression system

stood alone in this country as the only efficient means of obtaining oil from seeds. The earlier difficulties that were met with in this process, *e.g.*, unsatisfactory solvents and inferior distilling plants, did much to retard the progress of the system, even after solvent plant meal became a recognised ingredient of compound feeding-stuffs. Whilst for general suitability a specially prepared petroleum spirit has been considered the best solvent, more recently trichloroethylene has come into prominence, and it appears to be agreed that its non-inflammable character, its greater penetration, its smaller losses on recovery and the increased production per plant unit, with lower steam consumption for its evaporation, make it preferable to petroleum spirit. Its suitability for the production of edible oils is challenged, and this fact, coupled with a relatively high cost, has so far operated against any extended use of this solvent. A comparison of the two systems of extraction shows prominently the advantage of the solvent method in point of oil yield. With seed residue which cannot be used for cattle food and is practically refuse, the high yield of oil given by the solvent system leaves it without a competitor in the treatment of such seeds. With linseed the solvent system offers no advantage over the Anglo-American press beyond requiring less labour. One would imagine that there would be an advantage in the extraction of wood oil, provided the solvent plant could be used in the country of origin and the nuts could be brought into a suitable form, whereby rapid and complete extraction were possible. The following table shows a comparison of output and labour required for the three processes :—

	Output. Tons per week.	Men required for shift.
Cage presses (mov. box)	270—300	5—6
Three batteries, Anglo-American press.....	270	10
Four extr. solvent plant.....	260—280	3—4

Although the extraction process is not in use for linseed, yet in the case of soya-bean oil agriculturists now recognise two types of soya-bean cattle food, soya cake and soya meal, the former being the product of pressing and the latter of solvent extraction. Eddy ⁷ concludes that with improvements constantly being made in processes and plant, and with the light that is being thrown on the subject by careful study and discussion, the future of the vegetable

oil industry lies in the adoption of the extraction process. It must be pointed out that the colour is darker and the acidity higher in the case of solvent extracted oils, but these oils are said to be easier to refine if treated when dissolved in the refining spirit.⁸

China Wood Oil.—China wood oil has been coming into American and European markets in steadily increasing quantities for the last fifteen years, the demand and price growing larger as manufacturers became more acquainted with its value in the varnish, enamel, paint and linoleum industries. The lack of uniformity in the grades received, due to the crude and unscientific methods of production used by the Chinese, had seriously restricted its application. During the last few years the leading British firms in Hankow have expended a considerable amount of capital in erecting improved refining plants and organising systems which will ensure supplies of a reliable product for manufacturers.

There are two varieties of the oil, red and white. The white variety is largely exported, whilst the red is consumed in China, and the residues from the white may be manufactured into the red variety. The trade names and districts of origin are three in number: (1) Chwan Tung oil, from the Sze-chuan Province; (2) Chi Low oil, from Hunan Province; (3) Siang Tung oil, from Hupeh Province. The Sze-chuan Province gives the largest supply, and the export of the oil is concentrated at Chiangkiang and Wanh sien. The Hunan oil supply is concentrated at Changteh, whilst the Shensi and Hupeh supplies are centred at Hankow. The trade is usually at Hankow, but the oil can be also obtained direct from the above-named places as well as Shasi and Ichang. The producer of the oil sells to a native oil firm, which sells to other firms doing a large business in future deliveries, and these in turn sell to exporters, who refine the oil by running it into open vats heated by steam coils till most of the moisture is expelled.

The methods of extraction are two in number: (1) pressing at high temperatures; (2) pressing at the ordinary temperature. In some districts the tung seeds are dried in the sun, powdered between stones and separated from the seed by sieving, or the husk is removed by roasting the fruit on iron pans till it bursts. When the nuts are separated by hand, the dry husk is used as fuel. The ash is sold to the native potash-maker, who extracts the potash in a crude manner and sells it to the native indigo buyers. The powdered tung seeds are heated in a pan for 20 or 30 minutes, and the mass is taken out, wrapped in a piece of hemp cloth and pressed for half an hour. The grinding mill and the seed presses are of the simplest

construction: a stone mill worked by oxen, and antiquated wedge presses with iron frames, having straw packing on the outside, on which the meal is placed. About sixty of these frames are stacked in the press and the pressure is supplied by a system of driving in wedges. The oil drains through the straw and drops into a pan at the bottom of the press. The oil so obtained is called first-pressed oil. The meal is again powdered, heated and pressed as before. The oil so obtained is second-pressed oil. The oil of each pressing is allowed to settle separately and filtered after some time. The kernels contain about 53 per cent. of oil, but the practical yield of oil amounts to only 40—41 per cent. It has not been found profitable to substitute for the native plant modern hydraulic presses (Lewkowitsch).⁹

In the pressing at ordinary temperatures the tung seeds are dried in the sun, powdered, and the skin is removed as in the first process, but after sieving the mass is pressed without being heated over a fire. It must be mentioned that previous to pressing in both methods the meal is steamed by being placed in wicker baskets suspended over boiling water.

In some districts the fruit is gathered and piled in stacks, covered with straw or wet grass and allowed to ferment until the husk is easily removed. The partly decomposed husk is used as a fertiliser. The oil produced by pressing at the ordinary temperature is pale in colour and is the oil of export. The higher temperature pressing gives a much darker variety. The oil is prepared for shipment to the port, e.g., Hankow, by being run into wicker baskets lined with varnished paper, and in this form is received by the native wood-oil merchants, who pass it on to foreign merchants, who carry out the refining. The oil is shipped either in barrels or in tanks, and the sampling requires careful supervision.¹⁰ The refuse of the refining is returned to the dealers, who sell it to the natives to be mixed with gypsum for caulking junks and sampans. The worst part of the refuse is burnt for Chinese ink. The meal is poisonous to cattle but may be used as a fertiliser. The term pale has no special significance for tung oil, and the colour after polymerisation is a better guide.¹¹ Reference may be made to an excellent paper by E. H. Wilson¹² on the cultivation of the *Aleurites* in China, to a communication by F. H. Rhodes and T. J. Ling,¹³ also to an article in the *Chinese Economic Bulletin*.¹⁴

The demand for the oil has increased so much that its cultivation in other countries has been under careful investigation. Experiments were started in 1914 in the cultivation of seed in the Southern

States of North America. In 1923 an inspection was made of the plantation in Gainesville, Florida, which was planted in 1912. There are at present 200 tung-oil trees and 2000 tung-oil seedlings under examination at the Gainesville experimental station.

It is absolutely necessary that the nuts should be planted in the dormant season (November, December and January); otherwise they get an early start and sprout up with a thin stem. Rough estimates indicate that 300 lb. of the fruits will produce about 140 lb. of seed. As the "white meat" constitutes about 60 per cent. of the seed, and the "meat" usually contains about 60 per cent. of oil, this would indicate a yield of 50 lb. of oil. One of the trees at Gainesville has produced in one year over 90 lb. of shelled seed, equivalent to about $3\frac{1}{2}$ gallons of oil. It is not expected that the average tree will yield that amount, but it is believed that a tree 4—8 years old will yield sufficient seed to produce a gallon of oil. It is estimated that maximum production will be attained at the end of the tenth year. No plant in Florida is less subject to disease and to insect attack than the tung-oil tree. It may be of great benefit to certain parts of North Central Florida, where citrus fruit cannot be raised successfully and where cotton has been affected by the boll weevil. The examination of Florida tung-oil nuts (1920) showed that from 97 lb. of nuts the percentage of shells was 55, percentage of "meat" 45, percentage of oil in "meat" 49. The oil on analysis was shown to be of very good quality. Tung-oil fruits from Tallahassee (1920 crop) showed: outer husk 50 per cent.; inner shell 20 per cent.; "meats" 30 per cent. Again the oil was of very good quality. Fruits from Batesville, Ala.: outer husk 48 per cent.; inner shell 19 per cent.; "meat" 32 per cent.; oil in "meat," by extraction, 64 per cent. A sample of oil from the 1922 crop at Gainesville was of very pale colour and high quality.¹⁵

A recent communication by H. A. Gardner on Crushing Experiments on American tung-oil seed showed that seed received in a damp condition, when crushed in the shell, yielded a dark-coloured oil, owing to the slime from the shell being carried into the oil during pressing and the heating which occurred during the pressing. If the seed were properly dried, either in the sun or on flat trays in heated rooms, a very light-coloured oil was obtained on pressing. With an Anderson Expeller working on uncooked seed a high yield of light-coloured oil was obtained, only about 4.5 per cent. of oil being left behind in the cake. The quality of the oil was excellent and the yield was 24.1—28.6 per cent. The

cold pressed oil showed yellow 35 and red 3.3 in the Lovibond tintometer, and the hot pressed oil yellow 35, red 4—5.3. The characters of the various samples of oil obtained were normal (*J.*, 1924, 43, 639B). It is estimated that about 50,000 acres would require planting to satisfy the American market. Regarding the cultivation of the tung-oil tree in India, the matter is still in the experimental stage.

In 1906 the export from Hankow was nearly 29,000 tons, and the amounts exported between 1913 and 1918 from Hankow and Wuchow are given as follows:—

	Hankow.	Wuchow (Canton).
1913	40,917 tons	1526 tons
1918	28,214 „	5858 „
1919	36,500 „	—

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CHAPTER V

REFINING AND BLEACHING OF LINSEED OIL

REFINED linseed oil is an oil which has been treated by mechanical and chemical means to remove not only the mucilage, but most of the colouring matter, and it is generally used for grinding with white pigments. Some grinders maintain that for most pigments less refined oil, as compared with raw linseed oil, is required to pug up the pigments before grinding.

Varnish Oil.—Linseed oil after extraction from the “meats” in the pressing process contains foreign matter called “foots,” derived from the seed. The more unripe and the damper the seed the greater is the quantity of “foots,” especially when excessive heat has been applied in the kettle before crushing. They are removable, together with some of the colouring matter, by prolonged settling or tanking. The “foots” are partly albuminous and partly of a carbohydrate nature; the former elements are chiefly removed in the first stages of tanking, whereas the latter require a heat or special treatment for their complete separation. The water in the oil, derived from the steaming of the linseed meal during the crushing process, partially separates out on storage, but some is retained by the albuminous and carbohydrate mucilage, the latter of which is soluble in water. When linseed oil is heated rapidly to 260° the moisture is expelled and the protein and carbohydrate mucilage separate as gelatinous “spawn,” or the oil “breaks.” Generally the colour is improved if a well-matured oil be heated, because the mucilage removes much of the colouring matter. The quantity varies with the nature of the oil and with its age. If linseed oil be heated slowly up to 260° the separation of the mucilage is retarded, possibly due to the increasing viscosity of the oil during the slow heating; on the other hand, if the oil be allowed to cool very slowly, part of the coagulated mucilage redissolves and cannot be separated by centrifuging. When drying oils are stored there is a slight increase in the specific gravity and acidity.¹

Mucilage.—The foots which separate out on heating commercial linseed oil contain 8.6 per cent. of dry mucilage and 91.4 per cent. of oil. Thompson² found that a sample of freshly-expressed oil, heated to 400° F., gave 0.277 per cent. deposit; one of the authors finds that if Calcutta linseed oil (15 c.c.) be heated to 260° in a test-tube allowing a rise of 50° per minute and centrifuging 1 hour after heating, while the oil is still warm, the percentage of mucilage varies from 3.6 per cent. to 4—6 per cent. by volume. If the oil be allowed to stand over-night before centrifuging, the amount of deposit will drop to 0.3 per cent., or to nothing, showing that either

the mucilage has redissolved partly in the oil on cooling, or that its degree of dispersion has been modified. Thompson found that the mucilage (0.277 per cent. by weight of the oil) contained 47.79 per cent. ash, consisting of 20.96 per cent. CaO , 18.54 per cent. MgO , and 59.85 per cent. P_2O_5 . Ingle ascribed to the mucilage a content of 14.9 per cent. ash, of which 2.7 per cent. consisted of P_2O_5 . The composition of the mucilage depends on whether the oil has undergone a preliminary refining process in the factory, or whether both protein and carbohydrate mucilages are present. From the experience of one of the authors linseed oil of good quality contains no nitrogen, while Thompson found less than 1 per cent., and owing to the large amount of bases present, he did not consider that the phosphorus present could be due to lecithin. In some commercial linseed oils alumina and silicates, due to partial refining with fuller's earth, are found in the ash obtained from the mucilage. The statement that oxidation of the mucilage occurs before that of the oil requires confirmation, likewise the statement that the fish-like smell of certain linseed oils is due to the oxidation of the lecithin present in the albuminous matter in the oil. The assertion of Niegemann³ that the mucilage consists essentially of protein material is not borne out by Neville's investigations.

The nature of the non-nitrogenous mucilage has been investigated by Hilger⁴ and Neville.⁵ The water-soluble mucilage is of a carbohydrate nature, to which Hilger ascribed the formula $2(\text{C}_6\text{H}_{10}\text{O}_5), 2(\text{C}_5\text{H}_8\text{O}_4)$, or a galactose and pentosane substance from which dextrose, galactose, arabinose and xylose were separated. The mucilage contains calcium, magnesium and iron carbonates and phosphates in considerable quantity. Neville extracted the mucilage from linseed by cold water and found it to be 6.28 per cent. of the seed treated. If the extraction be performed by 1 per cent. sulphuric acid, the amount of protein matter obtained is appreciable, whereas water extraction yields a solution which gives only a slight precipitate with phosphotungstic acid. This will account for the occurrence of protein material in the mucilage in the presence of acids. The carbohydrate precipitated by alcohol from aqueous solution is insoluble in all organic solvents. The aqueous solution gives a gelatinous precipitate with salts of heavy metals. Neville was able to isolate derivatives of galactose and pentosan sugars, and he considers that water-soluble mucilage is well described by the term muco-cellulose of Cross and Bevan, being a carbohydrate showing all the characteristics of hydrated cellulose. Reference may be made to the mucilages obtained from Japanese seaweeds, known as "agar-agar" and "Japanese isin-

glass" and Irish moss jelly, which contains the anhydride fucan, $C_5H_7O_4(CH_3)$, from which a methyl-pentose, fucose, $C_5H_9O_5(CH_3)$, is obtained on hydrolysis. The mucilages of certain varieties of seaweed from Japan are stated by E. Takahasi⁶ to yield pentose and hexose sugars on hydrolysis. It is of importance to state that the water-soluble mucilage of linseed oil is not acted on by enzymes or by bacteria (Neville), so that it can play no part in causing rancidity of the oil. The presence of mucilage in linseed oil is generally considered to be detrimental, and its removal requires a refining process. The actual weight is very small, but its oil absorption and its power to absorb water are high. Suspended material in the oil settles slower when mucilage is present and the water absorbed has an emulsifying action, which retards the brightening of a varnish mixing. Its effect is perhaps greater in the thickening of oils, especially those required in printing inks. At the same time it may act, as in the case of gum arabic in water, as a protective colloid for metallic driers and so serve as a promoter. The removal of the protein-containing mucilage is of greater importance than that of the carbohydrate variety, and a reasonable period of tanking is sufficient to remove this modification, for the non-nitrogenous part interferes only slightly with the properties of a varnish oil. In fact, removal of the carbohydrate mucilage *by heat* from a previously tanked oil lengthens the time required for thickening the clarified oil. If it be impossible to allow the protein mucilage and water to drop out in a process of tanking, then recourse must be had to one or more of the refining processes described below. There are several methods used by a varnish-maker in the refining of the oil. Fuller's earth, caustic soda and sulphuric acid are commonly employed. Other substances proposed are boric acid, borax, fused sodium carbonate, slaked lime, magnesium oxide, litharge, zinc chloride (the oil requires subsequent washing to remove hydrochloric acid formed), dried white copperas ($ZnSO_4 \cdot H_2O$), zinc resinate, calcium resinate and calcium carbide. One of the authors⁷ has put forward a method for removing the carbohydrate mucilage by churning with solutions of 10 per cent. sodium chloride or aluminium sulphate. Sulphuric acid (1 in 10) can also be used. Ten per cent. ammonium alum causes a coagulation of the mucilage so that the oil does not brighten easily. It is advisable to give a treatment with a second quantity of salt solution so as to ensure the removal of the mucilage. It is unnecessary to give the oil a washing with water, and it is inadvisable to do so because of the persistent cloudiness which ensues.

The fuller's earth treatment is perhaps the best known method employed. Fuller's earth was in former days used extensively by "fullers" for the cleaning or "fulling" of woollen goods, owing to its property of absorbing grease. The two main producing countries are Great Britain and the United States (70,000 tons in 1922). In England it is mined at Reigate and Mitfield in Surrey, in Somerset and in the vicinity of Bath. The English output in 1920 was 29,000 tons. Two varieties are known, the yellow and the blue earth, and they contain 53—60 per cent. SiO_2 ; 10—20 per cent. Al_2O_3 ; 4—9 per cent. oxides of iron; 1.25—3.26 per cent. MgO ; 0.5—3.17 per cent. CaO ; and the loss on ignition varies from 3.56 to 24 per cent. The upper layers of the deposits are brownish-yellow, while the lower and unoxidised are greyish-blue. All the deposits are of secondary origin and are sedimentary, possibly from the decomposition of augite and hornblende. In the preparation of the earth overheating must be avoided, as the removal of the combined water is supposed to be detrimental with English earths, although the American earths are not so affected. The fineness should be 100—120 mesh. In the U.S.A. there is a great demand for the earth for bleaching purposes in the petroleum industry. The absorbing property is due to the so-called colloidal portion of the earth, which is apt to differ widely in action on colouring matters present in oils and fats, and earths which efficiently decolorise vegetable oils containing one type of organic colouring matter are quite useless for mineral oils. It is customary to warm the material together with the earth, so as to expel the air and to increase contact with the particles of the earth, and to reduce the viscosity of the material. The colloid activity of the earth deteriorates above 150° . The English variety is preferred to the American in the refining of edible oils. Cotton-seed oil requires 1.5 per cent. of its weight of earth, arachis oil 1 per cent. and coco-nut oil 0.5 per cent. The total losses on refining are 1—2 per cent.⁸

Deposits have been found of an aluminium hydrosilicate which possesses a bleaching power superior to fuller's earth.⁹ It is stated to absorb 45—60 per cent. of its weight of oil, against 100—200 per cent. for fuller's earth. The earths Frankonite, Siltonite and Tonsil are the most efficient. With linseed oil, previously warmed to 90° , 5—10 per cent. Siltonite F. will give an almost water-white product in 40 minutes. J. A. Pickard¹⁰ states that linseed oil, which does not break on heating, can be obtained by filtration through a stream line filter.

Plant for Refining Linseed Oil with Fuller's Earth.—This consists essentially of (a) a vortex mixing kettle for mixing the fuller's earth with the oil, (b) a filter-press for subsequently removing the oil from the earth used, together with all the suspended matter and mucilage. The mixing kettle is of a design that ensures the most intimate mixing of the earth with the oil. The oil, if necessary, is previously heated in another special tank to the required temperature before being run into the kettle. The actual temperature varies with the oil and with the factory conditions. The kettle is usually jacketed on the bottom only, and this gives sufficient heating surface to enable the requisite temperature to be maintained with facility. If necessary, the kettle is provided with a much larger jacket as a heating surface, so as to heat the oil up to the required temperature. A feed pump is fitted, self-contained, to the filter-press in order that the oil may be filtered in the shortest possible time. The earth used varies from 2 to 5 per cent. of the weight of the oil.

Method of Treatment.—The oil previously heated, if necessary, is run in to within 4 inches of the top cover of the kettle; the mixing gear is started to agitate the oil and to drive off any moisture. The earth (Florida Earth), which should be quite dry—a very essential point—is added when the required temperature is reached (not above 190° F.), and intimately mixed with the oil. It is best to determine the most suitable temperature and the amount of the earth by previous experiments on a small scale.

The pump is started and the oil filtered through the press. As soon as the filtering operation is finished, the earth should be steamed out to recover as much as possible of the oil contained in it, which is accomplished by opening the steam valve on the head of the filter-press and allowing live steam to blow through very quickly, until the oil ceases to flow from the outlet of the plate. It is important that the steam be dry, and to this end a drain cock should be fitted on the steam pipe just before it enters the filter-press. Immediately after steaming out, the press is opened and the plates are separated from each other so as to leave an equal space between them. If this be done, the heat contained in the iron plates will dry the cloths as well as the deposit of earth, so that the latter can be readily removed without taking off the plates, leaving the cloths quite clean. It is advisable to keep separate the oil steamed out of the earth, as it may not be equal in quality to the oil filtered before steaming. Bone charcoal will also remove the mucilage, and many refiners prefer to mix the charcoal

and earth, as they maintain that the mixture facilitates the filtration of the oil.

Alkali Method.—Perhaps this is the most successful way of treating linseed oil. The process consists in nearly neutralising the free acids of the oil with a solution of caustic soda, or soda ash, or a mixture of these two, the soap formed carrying down the mucilage, which can be filtered off. The method of treatment varies greatly. Some oil refiners prefer to use all the alkali solution cold and then to warm the oil; others prefer to warm the oil first and then add the alkali. The strength of the alkali solution varies. A 5 per cent. caustic soda solution or 6 per cent. soda ash gives good results. Some refiners use solutions double the above strength. The amount of the free acid in the oil varies, and if it exceeds 1 per cent. the stronger alkaline solutions are desirable. About 3 lb. of caustic soda are required for every 1 per cent. of free acid in a ton of oil.

The alkaline solution should be added slowly to the oil with good agitation. Neutralisation only of the free acid, and not saponification of the oil is required. The oil should, if warm, be allowed to cool to 15°. If the oil after removal of the foots can be cooled down to 0° by a brine solution of a refrigerating plant, and then quickly filtered, an excellent varnish oil is obtained. Schwareman¹¹ states that alkali refined oil should be well washed. If a neutral oil be desired, the free acids should be almost completely neutralised, and the oil washed with warm water. It is not advisable to boil or heat to a high temperature, as this may cause free acid to be regenerated in the oil.

Sodium hydroxide removes, not only the free fatty acids, but also the phosphatides and colouring matter from vegetable oils, and is used universally in the refining of cotton-seed, soya and corn oils. The details of the treatment applicable to linseed oil are given below. Sodium carbonate removes free fatty acids, but relatively little of the colouring matter and the phosphatides. Lime cannot be used, because of emulsion troubles. Hulme discovered that the treatment of cotton-seed oil with a solution of boric acid precipitates a coloured body which is a phosphatide. According to B. H. Thurman¹² the boric acid precipitate from cotton-seed oil represents 1.445 per cent. of the weight of oil treated and contains fatty acids representing 0.957 per cent. of the original oil, whilst the non-fatty matter, comprising proteins and colouring matter, forms 0.578 per cent. of the oil, whereas, in contrast to the boric acid treatment, the cotton-seed oil soap-stock obtained as a deposit by agitating the oil with caustic soda is found to represent 11.8 per

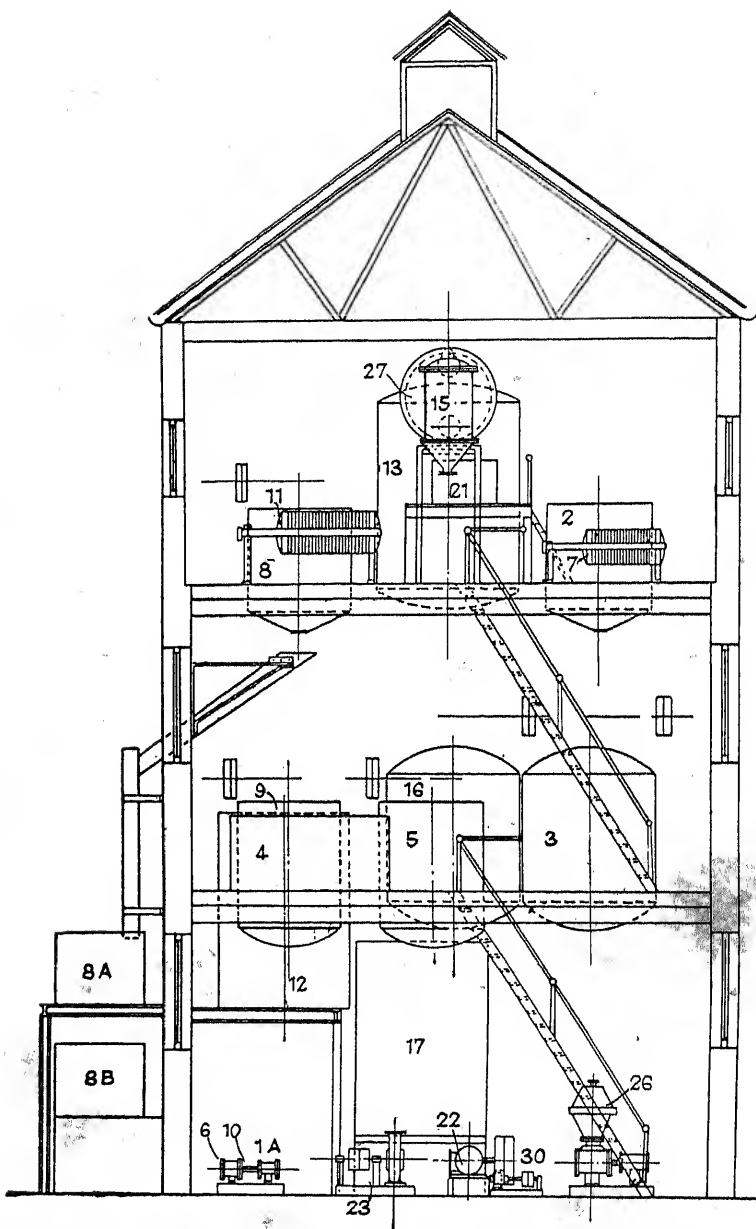


FIG. 17.—Edible Oil Refinery (Rose, Downs and Thompson, Ltd.).

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|---------------------------|-------------------------------|----------------------|
| 1. Melting-out Tank. | 8A. Soap Splitting Tank. | 17. Barrelling Tank. |
| 1A. Oil Pumps. | 8B. Fatty Acid-settling Tank. | 18. Sump and Wier. |
| 2. Slimes Treatment Tank. | 9. Second Bleacher. | 19. Superheater. |
| 3. Vacuum Drier. | 10. Filter-press Pump. | 21. Caustic Tank. |
| 4. Slimes Boiling Tank. | 11. Filter-press. | 22. Dry Vacuum Pump. |
| 5. First Bleacher. | 12. Clean Oil Tank. | 23. Water Pump. |
| 6. Filter-press Pump. | 13. Deodoriser. | 26. Wet Vacuum Pump. |
| 7. Filter-press. | 15. Barometric Condenser. | 27. Preheater. |
| 8. Neutralising Tank. | 16. Vacuum Cooler. | 30. Oil Pump. |

cent. of the original oil. Fifty per cent. of the soap-stock is derived from the oil, and the remainder has its origin in the water and soda of the solution used. The non-fatty matter formed 1.37 per cent. of the original oil, more colouring matter being thrown down when a boric acid solution is employed. The removal of the free fatty acids by the alkali is complete. The soap-stock produced in the caustic soda treatment is either sent to the soap-maker or made into black grease. The Bataille process¹³ has been in use since 1915, and has the advantage of eliminating washing of the oil, as the soap-stock separates out in a dry state without leaving soap dissolved in the oil, the moisture having been previously removed by evaporation under diminished pressure at 55°.¹⁴ After treatment for from 1½ to 3 hours, the oil, previously exactly neutralised by caustic soda, is sent to ordinary refining tanks to settle. It retains approximately 0.01 per cent. of free fatty acids.

A varnish oil treated in this manner may still deposit slight mucilage on long standing, but the oil will stand the "heat test."

As the free acids are low, the oil will thicken quicker and bleach better on heating up to high temperature for stand oils.

The presence of proteins, mucilage and certain bacteria and fungi develops rancidity if the oil be exposed to air, and more especially in the case of edible oils, which start decay of the oil or the paint made from it. Varnish oil is to be strongly recommended for stand oils and oils for printing works.

The process is simple and the cost not excessive. At least the oil is well worth the slight extra cost, compared with raw linseed oil, which may contain an excessive amount of mucilage.

Lime and magnesia have been used, but from the experience of one of the authors are not so successful as the soda method of treatment.

Sulphuric Acid Method of Refining Linseed Oil.—The plant consists of: (1) large lead-lined wooden vats with suitable stirrers or emulsifiers. The lead should be the purest and the joints and seams lead burnt. As a rule 10 lb. lead is used to line the tanks. Air agitation may be applied; it has been found that the "foots" do not settle so well when it is employed. (2) A second tank, slightly larger, fitted with a steam pipe with efficient spreader with small holes, to boil the water with open steam in order to wash the oil. Ten tons of oil is the usual quantity that is refined in one operation. The oil is pumped into the top tank, and the stirrers are started. Some refiners prefer to heat the oil before adding the acid, but it is not essential. The sulphuric acid, the

C.O.V. of commerce, which should be of good quality and free from nitrous or nitric acids, is slightly diluted with water. The strength varies with the oil to be refined. The proportions are from 7 to 4 of acid to 1 of water. It is advisable to try beforehand what strength of the acid is most suitable to refine the oil to be dealt with.

The aim of the refiner is to add just the right amount and correct strength of acid to attach and char the mucilage and colouring matter without burning or impairing the colour of the oil. As linseed oil is easily burnt, the whole operation needs care and experience.

The acid treatment requires washing of the oil to remove sulphonated glycerides and fatty acids. The presence of sulphonates may cause thickening and development of yellow colour of paints. The acid-treated oil is generally considered to be inferior to alkali-refined oil for paints and varnishes.

The acid should be added in as fine a stream as possible. At first it absorbs the free moisture, and the oil turns green or greenish-blue. The colour is a good guide to the refiner. The mucilage and colouring matter will coagulate in small brown flakes, gradually becoming larger. At this stage the greatest care must be taken, as here lies the danger in adding too strong or too much acid.

The oil is tested by dropping a sample on a clean white saucer or tile and noting its colour. When the flakes leave the oil clear and it is almost colourless, no more acid is necessary. The oil is well stirred and about 20 to 40 gallons of water are added. This swells the "flakes" and also prevents the acid from having any further action on the oil. The amount of the acid varies, but as a rule about 1 gallon to $1\frac{1}{2}$ gallons of acid should be sufficient for every ton of oil.

The oil is allowed to settle over-night, and the next day it is run from the deposit of acid foots into the second washing tank, in which about 500 gallons of water are boiling, and the whole is brought to a gentle boil with the open steam. This is allowed to settle for 1 hour and the water and acid in solution are run off. More water is added and the whole again boiled. A third boiling may be necessary. Some prefer a good steaming instead of a third washing.

Care must be taken in the washing to avoid emulsions, which are sometimes caused by mustard oil present, due to bad screening of the linseed.

After all the water has been run off, the oil is beaten by revolving

blades, which dip about 4 inches below the surface. These impart a shaking motion and greatly assist in removing the last traces of water. About 4 hours' "beating" should be sufficient. A sample of the oil should be bright and clear when cold. The oil is then run into the stock tank, which should also be lead lined. If necessary, the oil may be filtered through sawdust containing a little magnesia.

It must be stated that some linseed oils are impossible to refine to a good colour, and yet they may be commercially pure. The acid foots are best washed repeatedly with hot water in a small lead-lined tank. The oil obtained from the foots is of a dark brown colour, and contains free acids and sulphonated oils. It can only be used for very cheap paints, or sold for soap-making, or used in the distillation of oils and fats. The losses on refining should not exceed 1.5 per cent. of the oil.

Properties of Refined Oil.—These vary in physical and chemical characteristics only slightly from genuine raw linseed oil. The colour is paler and the free acidity may be higher.

A refined linseed oil should be free from foots or other visible impurities. The specific gravity at 15.5° should not be less than 0.93 and not more than 0.934. The refractive index (n_D) should not be less than 1.479 nor more than 1.4805 at 25°. The iodine value should not be less than 180 (Wijs). The acid value should not exceed 4 mgms. of KOH per gm. of oil, or 9 mgms. of KOH per gm. of oil in the case of acid-refined linseed oil.

Bleaching of Oils.—Linseed oil can be bleached by other methods :—

(1) *Sunlight.*—The oil is readily bleached in the sun, especially if it has been previously treated by the alkali or fuller's earth treatment. As a rule, the oil will bleach much better when the mucilage has been removed. The mediæval method used by Cenino Cennini has been referred to in the introductory chapter. The oil of the old masters was cold pressed, or pressed after having been slightly warmed, from pure seed, and then refined by exposure to sunlight and washing with water. For artists' purposes, the process is modified by shaking linseed oil with an equal volume of salt-water in a glass bottle containing sand, and exposing the mixture for a week to the sun, shaking vigorously each morning, and keeping the cork loose so as to allow free access of air. After a week of the daily shaking the bottle is left out of doors for five or six weeks. At the end of that time the salt-water will be full of a flocculent precipitate and the oil above will be clear. Further exposure will

render the oil almost colourless.¹⁵ By previous treatment with light the drying time of the oil is appreciably shortened.

Genthe¹⁶ describes the treatment of linseed oil at 80° in air exposed to light from a mercury lamp. Five kilowatt-hours are required for the bleaching of 100 kilos. of oil, and 5 per cent. of oxygen is absorbed.

(2) *Benzoyl Peroxide or Lucidol*.—Some oils are not easily bleached by fuller's earth or bichromate and sulphuric acid, *e.g.*, oil from olive husks. Bolis¹⁷ states that 100 kilos. of dark oil can be bleached by 150—200 gms. of benzoyl peroxide.

About 0.1 to 0.2 per cent. is added and heated up to 180—200° F., the oil being well stirred or agitated with a little air.

The peroxide slowly evolves oxygen, which bleaches the oil. Varnish oil that has been soda refined is the most successful to bleach with this reagent.

(3) *Bichromate Method*.—This method is not used in this country, but it has been employed in Germany. The process is not very successful, as it may impart a green colour to the oil and it is costly. Sabin quotes the following :—

Twelve and a half pounds of Bichromate of Potash or Soda in 60 lb. of water is the bleaching solution. This is heated by boiling in an iron pot, and 3½ lb. of powdered MnO₂ is added. While hot, hydrochloric acid is added, which is mixed into 1000 lb. of oil at 100° F., contained in a wood tank, and well stirred, and allowed to settle for five days (summer) or ten days (winter). The clear oil is drawn off and tanked for two months (summer) or four months (winter). The method is difficult and the addition of potassium chlorate is considered to be advantageous.

Other chemical methods have been proposed, *e.g.*, potassium permanganate or manganese peroxide and acids, calcium carbide, oxygen and ozone.

Bleaching with Ozonised Air.—Even with ozone, linseed oil cannot be bleached without increasing the gravity and the acid value. In the opinion of one of the authors, it is doubtful whether any better result can be obtained with ozone than with air. At least the ozone is not worth the extra expense.

Much has been written as to the value of ozonised air as a bleacher of vegetable oils. Success in the operation seems to lie in stopping the process at the moment when the colouring matter *only* is oxidised and destroyed. In the case of palm oil, ozonised-air-bleaching is stated to be a success if the above precaution be taken, and there is no tendency of reversion to the colour either in

the case of the oil itself or the soap produced from it.¹⁸ It is considered by some in the case of non-drying oils to be superior to the blowing process with air, either alone or in the presence of a suitable catalyst, *e.g.*, manganese and cobalt borates;¹⁹ on the other hand, 5 per cent. of hydrogen peroxide (30—60 per cent.) is said to bleach fats and oils, even when they are so deeply coloured as to be incapable of treatment by other methods.²⁰ The use of ozonators as described by C. H. Jones²¹ will depend essentially on the nature of the oil. During the bleaching by ozonised air there is an increase in the specific gravity, the viscosity and the acidity, with decreases in the iodine value and the time of drying. The rapidity of thickening depends on the temperature at which the oil is treated. Raw oil treated at 65—90° thickens rapidly, but the oil becomes darkened. When run at temperatures below 40°, the thickening proceeds more slowly and the oil is bleached. For bodying paint or varnish oils, a treatment of 6 hours is usually sufficient. For linoleum, the average treatment is stated to be 8—10 hours. After treatment with ozonised air (Ozonair plant) for 24 hours, a sample of linseed oil to which a trace of manganese drier had been previously added was almost colourless, and gave the following constant compared with those of linseed oil :—

	S. G.	Viscosity (glycerine =100).	I. V	A. V.	Drying time.
Unbleached linseed oil	0.9320	6.88	183.5	0.975	Wet in 6 days.
Almost colourless ozonised linseed oil	0.9470	10.35	170	3.8	Dry in 6 days.

The experience of F. E. Hartman²² is of interest. After referring to the use of the alkali (sodium silicate and caustic soda), fuller's earth combined methods, he states that when air containing 0.5 per cent. of ozone is allowed to act for 5 hours at 15—20° on the decanted and filtered oil in quantities of 15 gms. of ozone per gallon of oil per hour, a very pale oil is obtained. If the treatment be carried out at about 35°, marked oxidation of the oil results. Oil clarified by heating or a long-tanked oil will not mix well. The drying properties of all oils are enhanced. Commercial raw oil ozonised up to 8 hours decreased in drying time to 10 hours, but oil ozonised for 12 hours did not dry at all. Tabulated analyses of the ozonised oils showed that the oils took up more oxygen than that available

from the ozone employed, indicating that autocatalytic oxidation had also taken place. It is evident that the increase in acidity and decrease in the drying time will produce an oil that will be less suitable for grinding with pigments, and if heated to temperatures above 450° F. darkening occurs, which renders such oil of no advantage for varnish making. The advantages of the use of ozone are rather in the production of a bodied blown linseed oil. For paint grinding linseed oil bleached by the alkali process is much to be preferred, owing to the neutrality of the product.

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CHAPTER VI

BOILED, BLOWN AND STAND OILS

BOILED oil is linseed oil whose drying properties have been increased by heating it in contact with air with the addition of driers. In America the term boiled oil has the same meaning as in England. In France it is *huile de lin cuite*, in Germany *Leinölfirnis*, comprising a drying oil with or without thinners.

What takes place in the boiling cannot definitely be stated. Moisture is expelled and during the operation some acrolein is produced, so that there must be a slight decomposition of the glyceride, although the full amount of glycerine is usually obtained from boiled oil as compared with raw linseed oil (*vide* p. 154). It cannot be considered as a destructive distillation, and the amount of unsaponifiable matter is not increased to any appreciable extent. Polymerisation of the oil must occur to some degree; the driers act as "catalysts" or oxygen carriers for transferring the oxygen of the air to the linseed oil. If the oil be blown during heating, oxidation will ensue. Ingle found in cold boiled oil (steam boiled) and blown oil 13 per cent. of oxidised acids.¹

The actual method for the manufacture of boiled oil has undergone many changes; originally the oil was heated by direct fire to high temperatures, 500—550° F. (260—288° C.), when the driers were added. This process involved great risks of fire, so steam heating was adopted to obtain lower temperatures and to make the operation less dangerous. Air was blown into the oil to assist oxidation. The driers have been changed; the oxides of metals, as red lead, litharge, manganese oxide, umber, etc., have been displaced by the "soluble" kinds, namely, the resinates, linoleates, and latterly tungates of the metals. This replacement not only makes a better boiled oil, but effects a great saving of time and labour.

The search for the most active driers, which will help to produce the most durable boiled oil for paints, still continues, and offers scope for more investigation, together with more practical work on experimental exposure tests of paints and enamels.

The aim should be to obtain a boiled oil that dries in a reasonable time and under varying atmospheric conditions. The minimum amount of driers should be used. The oil when made up into paint should set to a hard and durable film able both to withstand dust and to stand abrasion. The raw drying oil should be bright and free from foots, of a good colour and smell, and as a rule the higher the iodine value of the raw oil the better is the boiled oil; oil from Indian seed is preferable to that from Plate seed.

Fire Boiling.—This method of manufacture is now not in common use. The whole operation demanded great skill and the utmost care. The danger of fire made it risky. Due to the high temperatures of boiling, it was not easy to produce an oil with the same colour and consistency. As a rule, the oil dried with a hard film and good gloss, but an excessive quantity of driers was used. The oil did not produce the best and most durable films.

Method of Manufacture (G. H. Hurst and Heaton, "Painters' Colours, Oils and Varnishes").—The oil was heated in set boilers of varying sizes, from 100 to 600 gallons, even as large a quantity as 5 tons being boiled in one pan. The boilers were made from wrought-iron plates; the bottoms, as they experienced the greatest corrosion, were made from separate plates, which were riveted to the sides. Suitable hoods conveyed the fumes away, whilst still allowing free access of air to the oil. The boilers were set over furnaces, and to safeguard against fire the fireplaces were placed outside the boiling-shed. The boiler was filled with oil to two-thirds its capacity, to allow sufficient room for expansion and frothing.

The oil was heated at first up to 350° F. (177° C.) to expel all moisture, then further heated up to a temperature of about 500° F. (260° C.), and at this temperature the oil appears to boil. The driers, consisting of a mixture of litharge and red lead, were sprinkled into the oil, which was gently stirred. The amount of driers varied with different manufacturers and in different countries, as great secrecy was observed. Five lb. of litharge per ton of oil, as stated by some authorities, seems rather low. Ingalls² gives as the composition of a good strong drying oil: 0.5—1.5 per cent. lead; 0.05—0.15 per cent. Mn; and cobalt slightly less than manganese. For 5 tons of oil an old oil boiler used about 42 lb. each of red lead and litharge. Sometimes a few pounds of oxide of manganese or umber were also added.

After all the driers were added, the oil was boiled to the right consistency, the time varying with the amount of oil, 5 hours being usually sufficient. After cooling, the oil was pumped into stock tanks to allow the "foots" to settle out, the amount of which is excessive compared with modern steam-boiled oil. The oil was of a dark colour, and considered by many to be poor in durability.

Waterproofing boiled oil made from Baltic oil by this direct fire heat is still often preferred. Soluble driers are now frequently employed.

It is surprising the strong preference shown by some users of boiled

oil for fire-heated boiled oil, also for dark boiled oils, as it is thought that such an oil must be fire-boiled.

Steam-boiled Oil.—The plant consists of large cylindrical tanks, or vats. Ten tons of oil are quite a usual quantity for boiling. Larger amounts, up to 20 tons, are boiled by some firms.

The tanks have either a steam jacket or a closed steam coil for heating the oil.

Coils are preferred, as they can be so arranged that the steam can be turned off, and water be run through to cool the oil. The coil or jacket should give sufficient heating surface to warm the oil up to 200° F. (93° C.) within 4 hours. Steam at low pressure, about 20 lb. and superheated, is better than ordinary steam at higher pressure. A good steam trap is essential. Air is admitted by a pipe with an efficient spreader at the bottom of the tank. This spreader should be perforated with a number of small holes to obtain fine streams of air in the oil.

The air is obtained from a powerful blower, and it is best to pass the air into an accumulator to give a steady pressure of air. The accumulator should have a pressure gauge, as well as a safety-valve to blow off at a set pressure.

A plentiful supply of air is essential, and the oil must be vigorously blown, not merely agitated. Many manufacturers err in using an insufficient supply of air.

The pressure of the air should be more than sufficient to break through the usual frothing. Mechanical stirrers are sometimes fixed to assist to break the froth and stir the oil. Stirrers can be dispensed with if a powerful blast of air be blown into the oil.

The fumes, which are irritating to the eyes, must be conveyed by suitable means to the base of a chimney-stack or, if possible, burnt in a small specially built furnace. Care should be taken that the fumes cannot back-fire through to the oil during boiling, as the fumes from boiled oil are very inflammable. A suitable thermometer and small sample cock should be conveniently placed for noting the temperatures and taking samples for testing.

Manholes at the bottom and top of the tank are built to allow of admission for cleaning the tank, coil and spreader, and, at the top, for admission of the driers. Both inlet and outlet pipes for delivery and pumping out the oil are required. The whole tank should be fixed upon solid masonry, because of vibration during the boiling.

The oil is pumped into the boiler to two-thirds of its capacity. Steam is applied either into the jacket or coil, and the oil should

reach a temperature of 200° F. (93° C.) before the blower is started. When this temperature is reached, the air is blown in and the driers are added; these are much the same as for fire-boiled oil. Sometimes sulphate of manganese is added. For 10 tons of oil the amounts of these driers are 84 lb. up to 112 lb. litharge, 28 lb. manganese sulphate. The soluble driers are now generally adopted. These are best admitted from a small steam-jacketed pan, where they have been heated with some raw linseed oil, thereby ensuring that the driers are properly absorbed and soluble in the oil to be boiled (this is an important point, as some driers, especially the resinates, are not completely soluble).

The air is increased and the steam regulated according to the particular colour required. As a rule, at 225° F. (107° C.) to 250° F. (121° C.) the steam should be shut off, and water run through the coil to cool the oil, because as the oil absorbs oxygen, considerable heat is generated. For dark-boiled oil the temperature may rise to 280—300° F. (138—149° C.), whereas for medium-coloured oil it may not exceed 260° F. (127° C.).

The whole operation in a modern plant should be completed in less than 3 hours after the addition of the driers. The oil is then pumped into settling tanks to allow the foots to settle and afterwards filter-pressed to ensure a bright, clear oil.

Extra Pale or Bleached Boiled Oil.—This should be paler than raw oil and suitable for use in white paints. It is most difficult to obtain an oil which will give satisfaction, *i.e.*, a bright pale oil with good drying properties. Sometimes one of these properties is sacrificed at the expense of the other.

It is most important to start with the proper quality of oil, which must be bright and clear and free from foots. An oil from Bombay seed gives excellent results. A good plan is to filter-press the oil before boiling, as the presence of mucilage causes subsequent darkening. A quick, reliable test for the selection of the oil consists in heating quickly a sample in a large boiling tube to 500° F. (260° C.), noting the colour of the oil and the amount and colour of the mucilage thrown out of the oil. The paler the oil and the mucilage the better will the oil bleach.

The procedure is very similar to that employed in the case of a dark-boiled oil; usually a separate tank is kept apart for the boiling of this oil, thus ensuring freedom from any discoloration from dark-boiled oil or its driers.

The oil is heated by a steam coil to 180° F. (82° C.). Air is gently blown in, and driers are added in small quantity to help to

bleach the oil. Heat is continued up to 260° F. (127° C.). It is not advisable to go beyond this temperature. The oil should now begin to bleach, and this is usually denoted by the temperature rising rapidly and by the production of a sharp, peculiar smell. The pressure of the air is now increased; steam is shut off and water allowed to run through the coils, so that the temperature gradually falls. When the desired gravity is obtained, the supply of air is reduced and the oil cooled by the water in the coil as quickly as possible. It is necessary to maintain the blowing of the air while the oil is cooling, otherwise the colour of the oil will suffer. As a rule, cooling to 150° F. (65° C.) with the air is safe. The rest of the driers can now be added, followed by a vigorous blowing to bleach the oil, and the oil pumped into settling tanks and then filter-pressed.

Various driers are used as bleachers; the most general are cobalt resinate or linoleate. Manganese borate dissolved in a little water with sufficient acetic acid to give a clear solution is fairly successful. For every ton of oil from 1 lb. to 4 lb. of cobalt resinate or linoleate is very effective. The remainder of the driers may consist of a mixture of fused or precipitated resins, linoleates or tungates of lead, cobalt and manganese.

Driers used for Boiled Oil.

Drier.	Percentage.	Mean temperature.
Litharge	0.5—1	400—500° F. (204—260° C.)
Red lead	0.5—1	—
Lead acetate	1—2	400° F.
„ resinate	1—3	220° F. (104° C.)
„ linoleate	1—2	—
Manganese dioxide	0.5	250° F. (121° C.)
„ hydroxide	0.25	400—426° F. (218° C.)
„ resinate	1—3	200° F. (93° C.)
„ linoleate	1—2	—
Cobalt acetate	1—2 lb. per ton	400° F.
„ resinate (2.7% Co) ...	20—40 „ „	180° F. (62° C.)
„ linoleate (8% Co) ...	10—20 „ „	„ „
Lead manganese resinate ...	2—3 „ „	„ „
„ „ linoleate ...	2—3 „ „	„ „

For the purpose of oil boiling it is important that the driers be of good quality.

Red lead and litharge are usually commercially pure and should

contain only a small trace of copper; powdered flake litharge is generally preferred. The oxides should be quite dry and finely ground. Manganese hydroxide is better than the dioxide and should contain 80 per cent. of manganese oxide. A good form of drier is the hydrate precipitated from the manganese chloride by caustic soda in dilute solutions, keeping the manganese salt in slight excess, so as to avoid free alkali, washing well, filter-pressing and drying at a low temperature; such manganese drier is efficient and readily soluble in oil or resin. Manganese borate should be the best quality, containing a high percentage of manganese, free from calcium and sodium sulphate, and soluble in weak acetic acid.

Cobalt acetate, carbonate and oxyhydrate are used in the preparation of the fused driers, whilst the sulphate is preferred for precipitated driers; for precipitated lead and manganese driers the nitrate or acetate of lead, and the acetate, chloride or sulphate of manganese and cobalt are used. The sulphate of manganese should be free from iron for driers for pale oils.

When dried sulphate of zinc is used, this drier absorbs the water given off during the thickening of the oil. The soluble driers for dark boiled oil, as stated before, are the resinates or linoleates of lead and manganese.

The resinates are not so good as the linoleates, as they are not so soluble, and the boiled oil on keeping is liable to deposit much of the resinate driers, more particularly lead resinate. The advantages of resinate driers are that they bleach more readily and less "foots" are deposited. It is not easy to produce a medium-coloured oil of a claret shade when linoleate driers are used. The latter are essential for a waterproofing boiled oil, because they give a more elastic film, which is not "sticky"; moreover the waterproofed materials will not adhere when rolled up.

For general purposes, a mixture of the fused resinates and linoleates of lead and manganese made together is recommended, keeping the rosin under 2 per cent. of the boiled oil. The allowance of 5 per cent. rosin is strongly criticised, as this amount is merely added to cheapen the cost of production. A combination of lead and manganese makes a better drier than either material used alone; lead drier alone tends to produce a boiled oil film which contracts on oxidation, whereas with manganese the film tends to expand. The best results are obtained when the ratio of the driers is 5 Pb to 1 Mn (as metals). Litharge is considered to give a more elastic film than red lead. For 10 tons of oil, a good drier would be:—

Rosin.....	2½ cwt. (G grade).
Baltic oil *	12 gallons.
Litharge	56 lb.
Manganese hydroxide	12—16 lb. (according to purity).

* Baltic oil should always be used for fused linoleates.

The rosin and oil should be heated to 550° F. (288° C.), whereby all the lower acids of the rosin are sweated off. The pan is taken off the fire or, if gas-heated, the gas is lowered. The driers are added very slowly with vigorous stirring. They are fairly quickly taken up, and when all have been added the pan is put back on the fire and gently heated until all frothing has ceased. The fused mass should be of a light brown colour.

A proper combination of the oxides, oil and rosin should be obtained. Herein lies the chief success of a good boiled oil. The driers should be used as soon as they are made, because exposure to air depreciates their value.

If the linoleate driers be selected, about 40 gallons of Baltic are used instead of the mixture of rosin and oil, and the same precautions are taken. Instead of manganese, cobalt is now preferred, and a combination of lead and cobalt gives an efficient drier for the paler shade of so-called double boiled oil. Such a drier may be made from :—

Rosin	1 cwt.
Baltic oil	24 gallons
Litharge.....	56 lb.
Cobalt acetate	10 „

Where a manganese boiled oil is desired, the linoleate (precipitated) is much better than the resinates, as manganese resinate alone is not considered in practice to be an effective drier.

A fused drier is preferred generally to a precipitated one, because the operation is much more simple and the cost is less. All precipitated driers are liable to contain moisture and should be fused before use to eliminate the water.

As driers of bleached boiled oil, cobalt and lead or manganese may be used.

White paint for inside work containing tetralin thinners may turn pink if manganese driers be used, and yellowing of white paint is considered by some authorities to be due to manganese (*vide p. 70*). It cannot be accepted that manganese boiled oil is the most durable. For cobalt driers, the acetate has been found most successful, as a pale drier can be obtained at low temperatures. For 10 tons of oil the following quantities may be used :—

Rosin	½ cwt.
Baltic oil (or wood oil)	30—36 gallons
Cobalt acetate	10—15 lbs. added at 400—450° F. (204—232° C.)

It is not advisable to attempt to make a drier with a high cobalt content. A cobalt drier has the disadvantage of its activity being sensitive to temperature variations. A combination of some lead is advisable, especially when the weather conditions are wet and cold (*vide* p. 104).

A combined lead cobalt drier for 10 tons of oil may be :—

Rosin	1 cwt.
Baltic oil (or wood oil) ...	24 gallons
Litharge	28—42 lbs. added at 400° F.
Cobalt acetate	10—15 " " 400—450° F. (204—232° C.)

Such a drier, especially if made from some wood oil, is found to be very successful for use as a pale boiled oil with white pigments, such as Timonox or titanium white, as these pigments made into paints retard the drying of the oil.

The precipitated driers of cobalt are very efficient driers, but the oil boiled with them does not eventually bleach so well as when the fused kinds are used.

J. S. Long and J. G. Smull² propose a method of controlling the boiling of linseed oil in the presence of lead and umber or Prussian blue such as is used for the enamels for patent leather, by determining the mol. wts. (by the F.P. method, using benzene) of samples withdrawn from the boiling oil from time to time, and plotting the boiling points against the mol. wt., the slope of the curve determining the end point of boiling. The mol. wts. are large numbers, and small differences in the boiling may be noted in a way not possible with variations noted in the volume. This method of control has been applied to linseed oil and has been extended to tung oil. In the following table the results are shown of some experiments which are of interest as showing some of the changes occurring when linseed oil is boiled with driers in contact with and out of contact with air :—

212 Gms. Linseed Oil (hand-stirred).

	Temperature.	Molecular weights.			
		Raw oil.	1 hr.	3 hrs.	3½ hrs.
No driers	271°	722	946	933	1091
PbO 0.33 gm.	271	722	1008	1765	1926
" 0.66 "	293	722	1852	Solid jelly	—
MnB ₄ O ₇ 0.40 gm. ...	271	722	865	1182	1464
" "	293	722	1147	Solid jelly.	—

In an Atmosphere of Nitrogen.

	No driers.		0.4 gm. PbO.	
	Mol. wt.	Iod. val.	Mol. wt.	Iod. val.
Raw oil	720	175.4	720	175.4
After 2 hrs. at 293°	981	145.2	953	136.5
„ 3 hrs. „ „	965	138.6	1020	125.8
„ 3½ hrs. „ „	1078	131.5	—	—

Changes in iodine value and acidity are shown in the following table :—

Sample.	Mol. wt.	Iod. val.	Free fatty acids per cwt.
Raw linseed oil	720	175.4	1.39
After 1 hr. at 298°	987	144.5	4.60 (80 min.)
„ 3 hrs. „ „	1511	114.5	3.97 (120 „)
„ 3½ „ „ „	1673	105.3	3.10 (160 „)

When oxygen is not excluded the rise in mol. wt. is very high and likewise the fall in iodine value is very marked. Precautions are taken to allow for change in mol. wt. when the oil is being cooled in bulk. The results are of interest, for they add to the scanty knowledge available on the changes occurring in oil boiling. The figures for the mol. wts. must not be considered of theoretical value, owing to the nature of the solvent employed and the acidity of the thickened oils. The values will be higher than expected.⁸

Properties of Boiled Oils.—Boiled oil is known under various names, as Double-boiled, Single-boiled, Pale-boiled and Extra Pale or Bleached Pale boiled oil. These are really trade names indicating differences due to colour and consistency.

The dark varieties have usually a stouter body. The specific gravity varies from 0.940 to 0.950, rising in some cases to 0.960. The oil should be bright and free from foots or mucilage. It should dry to a good film within 5—24 hours, a fair average is 12 hours under normal conditions. The oil should be free from any adulteration of mineral or rosin oils, other seed oils and fish oils. The amount of rosin either free or combined should not exceed 2 per cent. Much free rosin has many objections, and 7 per cent. will cause white lead paints to liver or feed.

The acid value should be under 6, and the saponification value 192—195. The ash or mineral matter should not exceed 0—5 per cent.

The iodine value is not of much importance, as it depends upon the gravity of the boiled oil and on the method of boiling. Few boiled oils of 0.945 gravity give iodine values much below 160. The unsaponifiable matter should not exceed that of raw oil (1.5 per cent.). The testing of the time of drying and toughness of the film should always be done with a sample of known purity and good quality. The craftsman's test of rubbing the dried film or scratching it with the finger-nail is in practice reliable.

The Adulteration of Boiled Oil.—Boiled oil is more adulterated than the raw oil. Perhaps because it is foolishly thought that the detection is more difficult. The usual adulterants are mineral or rosin oils, rosin, heavy distillates of white spirit, fish or other seed oils, as the market prices fluctuate. Mineral and rosin oils are readily detected by the saponification value and the amount of unsaponifiable matter; moreover, the greasy film on drying can be easily noted. A quick test is by Holde's method: In a large boiling test-tube, dissolve a piece of solid caustic potash (purified from alcohol) about the size of a pea in the minimum quantity of distilled water, and mix with 15 c.c. of absolute alcohol. Then add 10 drops of the oil. Boil for at least 2 minutes. Boil the alcohol well up the sides of the tube, in case any oil should adhere there, then add 50 c.c. of hot distilled water. A slight cloudiness will be caused by mineral or rosin oil, and as small an amount as 0.5 per cent. may be detected.

Rosin, if free, would increase the acid value. Heavy petroleum distillates will distil over if the oil be distilled with steam.

Fish oils are not easy to detect by smell, especially if the oil has been deodorised. Some boiled oils have an odour not unlike a fish oil. Fish oils may be detected in vegetable oils by the O. Eisen-schimi and H. W. Copthorne method.⁴ One hundred drops of the oil are placed in a test-tube with 6 c.c. of a mixture of equal parts of glacial acetic acid and chloroform. Bromine is added drop by drop until a reddish coloration remains. After 15 minutes the test-tube and contents are placed in boiling water. Most seed oils will clear completely in a few minutes, but with fish oil the cloudiness is permanent and a precipitate of an insoluble bromide will be found at the bottom of the test-tube. Five per cent. of fish oil can be readily detected. If necessary the metallic driers in boiled oil may

be previously removed by shaking with 10 per cent. nitric acid saturated with potassium nitrate, and washing the oil with warm water.

Other seed oils, as soya-bean oil, Niger-seed oil, are much more difficult to detect. As a rule they produce an oil that dries with a softer film, which is inclined to be greasy.

The above represents the strictly practical outlook on the boiling of oil. There is a considerable difference of opinion as to whether it is better to use raw or boiled linseed oil with pigments. In England the use of boiled oil is said to be on the increase. A discussion on the subject appeared in the *Decorator* of May 22nd, 1924. Some painters prefer to use no boiled oil, on the ground that it is a dangerous product and may lead to tackiness of the paint, others blend it with raw oil in the proportions of one-third to two-thirds, others mix a fairly large proportion with the paint for the final coat. For interior work, boiled oil is not to be recommended, but refined or pale boiled oil is desirable when zinc oxide is used for outside work, especially if a good mixing varnish be added. The discoloration on the fronts of stucco houses in the West End of London is considered to be due to the excessive use of boiled oil, which prevents the paint from drying hard and allows the adherence of dust and smoke. The question whether it is better to use raw or boiled linseed oil may be compared to the use of dry pigments against ready-made paints. Boiled oil will be free from moisture, from foots and clear only if obtained from a reputable firm. It is doubtful if painters using pure raw linseed oil and good Japan driers can make as uniform or as durable an oil film as when good boiled oils are used, because of the variation in the quantity of driers added by the painter. Ingle states that raw oil and driers instead of boiled oil have been found by painters to give cracked and blistered surfaces. On the other hand, the quality of a boiled oil is difficult to establish. The inferior varieties may be made on the bung-hole principle, where driers are introduced directly into the cold oil. In America there is the same difference of opinion, and the preference for boiled or raw oil varies with the locality. Specifications have been drawn up for the standardisation of boiled linseed oil, which is defined as pure, well-settled oil, boiled with oxides of manganese and lead, [the oil is not really boiled, as it is not heated much above 240° F. (115° C.)] and containing not more than 1 per cent. of rosin. The oil should conform to the following requirements, according to the U.S.A. Inter-Departmental Committee on Paint, Circular of the Bureau of Standards, No 82, 1922 :—

Boiled Linseed Oil.

	Max.	Min.
Loss on heating at 105—110°	0.2	—
Specific gravity at 15.5°/15.5°	0.945	0.937
Acid number	8.0	—
Saponification number	195.0	189.0
Iodine number (Hanus)	—	168.0
Ash, per cent.	0.7	0.2
Manganese, per cent.	—	0.03
Lead, per cent.	—	0.1
Time of drying on glass (hours)	20.0	—
Unsaponifiable matter	1.5	—

Another specification has been put forward by Amer. Soc. Test. Materials, 1921, 657, which also gives the methods of testing of boiled oil.

It would appear as if good quality dry linseed oil, free from foots, with the proper amount of driers, ought to be equal to good boiled oil, but for convenience the boiled oil is preferable, provided that it is of genuine quality.

Purity of Boiled Linseed Oil from North American Seed Serial Designation D11—15 (adopted 1915).

	Max.	Min.
Specific gravity at 15.5°/15.5°	0.945	0.937
Acid number	8	—
Saponification number	195	189
Unsaponification matter, per cent.	1.5	—
Refractive index at 25°	1.484	1.479
Iodine number (Hanus)	—	178
Ash, per cent.	0.7	0.2
Manganese, per cent.	—	0.03
Calcium, per cent.	0.3	—
Lead, per cent.	—	0.1

The unsaponifiable matter is estimated by Boemer's method ("Ubbelohde Handbuch der Oele u. Fette," pp. 261, 262).

Boiled Oil Substitutes.—These are many and vary in composition. No substitutes can compare with genuine boiled oil, and most are very inferior compounds. Some consist of rosin partly neutralised by lime and zinc oxide and dissolved in white spirit or distillate with some soluble driers and they may contain a little boiled oil.

Blown rosin oil is also used. This may dry fairly well, but sometimes it is not very soluble when mixed with raw oil.

The best substitutes are heavy-bodied oils, either heated or blown and thinned down with white spirit. They require careful use, as paints made from them may dry somewhat flat.

Blown Linseed Oil.—Linseed oil can be thickened until it has a gravity of 1000 and a high viscosity. The plant is the same as that for bleached boiled oil; the air supply must be plentiful, and great care must be taken if a pale result be desired. The raw oil is bleached by the minimum quantity of driers, of which cobalt resinate is very efficient. The oil is vigorously blown and the temperature of the oil should be kept at about 250° F. (121° C.), because if the oil gets above 280° F. (138° C.) the colour may be impaired. With a good source of air the gravity may be increased 10 points every hour. When the desired gravity or viscosity is obtained the air current must be almost stopped, and the oil cooled to under 160° F. (71° C.) by water running through the coil, otherwise the oil will lose its colour on standing.

If driers are to be added, they must be added below 150° F. (65° C.) and usually cobalt linoleate is preferred.

It is extremely difficult to obtain an oil with a low acid value. Blown linseed oil yields a series of volatile products, containing fatty acids, aldehydes, alcohols and aldehydic condensation products⁵ from carbon dioxide, formic acid and upwards.

Properties of Blown Oils.—Different gravities are required and up to 1000 are blown. The oil should be of a pale colour for paints and enamels. The acid value should be under 10. The viscosity may vary: an oil of 18 minutes Redwood viscosity at 200° F. is required by some firms, others require 14 minutes at 200° F.

The oil should be free from mineral or rosin oils, and other seed oils should be absent. The uses of blown oil are various: e.g., for mixing with refined oil for grinding white lead (some grinders use 5 per cent. of blown oil in the oil); for ochres and umbers—10 per cent. of blown oil is said to wet the pigments better. Added to varnishes, blown oils may impart better flowing properties. They are also combined with wood oil for cheap rosin varnishes. For enamels and high gloss paints it is not so satisfactory as "stand" oil, but the cost of production is less. A flat oil paint medium can also be made from blown linseed oil.

Polymerised Oils, Stand Oils and Lithographic Varnishes.—Linseed oil is thickened by heat to varying consistencies, and the oil is not usually blown—in fact the less the contact with air, the better the

thickened oil. The oil, heated to the ignition point of its vapours, is known as top-fired oil. Many demand lithographic oils to be made in this manner, especially for copper-plate printing. The quality of the oil is most important, as oil from Plate seed does not thicken so well as that from Indian-seed. Varnish oil is preferable, as the mucilage has been removed, also the acid value is less, and thus the oil thickens quicker. Baltic oil thickens well, but great care must be taken in top firing this oil.

Some makers use refined oil, but it must be free from mineral acids.

Plant for Stand Oils.—Eighty to 100 gallons are generally thickened in varnish oil pans, usually set upon fire furnace or heated by gas. As in fire-boiled oil, the fireplace should be outside the shed. Large pans are used for some oils. The pans are of copper, aluminium or enamelled iron; aluminium pans give very pale oils.

The oils are heated up to 500—550° F. (260—288° C.) and kept at this temperature until the desired thickness is obtained. Very stout oil may require 3 days.

It is very essential that the fumes should be removed, and they should not condense and run back into the oils, as they retard the thickening.

The loss in thickening varies. Coffignier states the loss to be :—

	Per cent
Thin	3
Middle	6
Strong	12
Extra strong	16

The colour, brightness and freedom from grease, body and strength are important properties.

Leeds gives the following constants (*J.*, 1894) :—

	S. G. at 60° F.	S. V.	I. V.	Oxidised acids.	Hexa- bromides.
Raw oil	0.9321	194.8	169	0.3	24.17
Tint oil	0.9584	197.5	113	1.5	—
Thin	0.9661	196.9	100	2.5	2.0
Middle	0.9721	197.5	91	4.2	—
Strong	0.9741	190.9	86	6.5	—
Burnt thin oil	0.9675	195.5	92.7	0.85	—

The stand oil for use in enamels must be bright pale colour, and of a low acid value; under 6 is excellent. (See Table, p. 58.)

The Merrill Patents (Kestner Evaporator and Engineering Co. Ltd.) for heating by oil circulation may be recommended in the production of stand oils. The system consists of circulating a specially refined mineral oil through an absorber, where the heat generated in the furnace may be obtained from oil, gas or coal firing. Fuel oil is considered most suitable. From the absorber the oil is passed into jacketed pans, containing oil to be thickened, provided with one or two inlets at the top and bottom of the jacket. Linseed oil may be heated quickly to 280° and kept constant. The advantages are: (a) fairly large jacketed pans may be used, and there is a low pressure in the jacket when compared with steam heating. The fire may be extinguished and the mineral oil circulated throughout the jacket to cool the stand oil when the desired thickness has been obtained. (b) The thickened linseed oil is of a low acid value.

Burnt Oil.—Those top-fired may produce a pale oil and will probably thicken quicker than an oil merely boiled. Great skill is demanded of the craftsman. The colour of the flame, as well as the slight rattle made by the burning, are the usual guides.

The difference between a boiled and a top-fired oil is difficult to explain. A top-fired oil will be paler in colour and less oxidised than a boiled oil.

For copper-plate printing the top-fired oils are insisted upon, as they are free from greasiness, and in copper-plate process the surplus ink has to be wiped off the plate without disturbing that left in the depressions.

For enamel oils the oil may be thickened by the addition of wood oil. Such a mixture will thicken quicker and a paler result is obtained. Up to 25 per cent. of wood oil may be used. The temperature must be carefully watched, as overheating may cause undue thickening or create excessive free acid.

The body or consistency of the stand oil up to strong grade is usually tested by the time a bubble takes to rise in a short narrow tube about 4 to 5 inches long and $\frac{1}{2}$ inch wide. For stronger oils the touch and feel or string are compared.

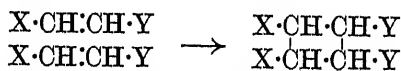
Polymerised Oils.—Much has been written on the nature of the polymerisation of drying oils. The subject has been dealt with fully in R. S. Morrell's "Varnishes and their Components" (p. 55, and J., 1915, 34, 105). The tables given on the next page show the reduction in the iodine values of the thickened oils, and emphasis must be laid on the fact that these values are disturbed by prolonged contact with the components of Wijs' reagent, and that

Baltic Oil at 250° in CO₂ Atmosphere (A. de Waele).

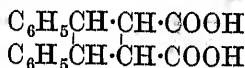
	Raw oil.	12 hrs.	56 hrs.	77 hrs. (oil solid).
S. G. 15.5°	0.9351	0.9423	0.9664	—
n_D^{25}	1.4808	1.4835	1.4936	1.4790
Iod. val.	196.6	175.2	119.8	—
Oxidised acids, per cent. ...	0.78	0.29	0.5	3.24
Solid acids (Fachini and Dorta's acetone method)	5.25	7.03	—	48.8
Iod. val. of solid acids	17.5	—	—	86.4

	Linseed Oil (Calcutta).		China wood Oil.		Poppy-seed Oil.	
	Raw.	28½ hrs. at 260° in CO ₂ stream.	Raw.	20 mins. at 240° in CO ₂ stream.	Raw.	Thickened in CO ₂ at 260° 28 hrs.
S. G. 15°	0.933	0.960	0.9405	0.950	0.9242 (18°)	0.9354 (22°)
n_D	1.4831 (19°)	1.4915 (19°)	1.5172 (14°)	1.5184 (15°)	1.4738 (20°)	1.4792 (22°)
Mol. wt. (in benzol)	805	1086—1704	707	1431	777	900—910
Acid val.	0.4	1.7	3.3	2.3	32—33	—
Sapon. val.	197—203	200	192.4	190—201	—	—
Iod. val. (Wijs)	185	118—134	165.8	148—171	180—180	115—132
Glycerol, per cent. ...	9.6	10.4	10.5	8.3	—	—
Cryst. hexabromide	33.5	—	—	—	—	—
Tetrabromo-acid	—	—	—	—	50%	6%
Solubility in acetone	100%	Sol. Insol.	100	Sol. Insol.	Completely soluble	Completely soluble
		41—45 42—46		46.6 47.5 72.2 27.8 (210°) (210°)		
S. G. 15°	—	0.9527 0.9763	—	0.9542 —	—	—
n_D	—	1.4846 1.4964	—	—	—	—
Mol. wt. (in benzol)...	—	904—75 {1788}	—	876	—	—
Acidity	—	75 0.2	—	2.47	—	—
Iod. val. (Wijs)	—	92—143 97—121	—	76—151 93—157	—	—

on transformation of the glycerides into either the methyl esters or corresponding acids the polymolecular character of the oils disappears. Ordinary polymerisation would be represented by a scheme :—

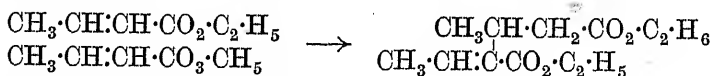


or cinnamic acid, $\text{C}_6\text{H}_5\text{CH}\cdot\text{CH}\cdot\text{COOH}$, to truxillic acid,



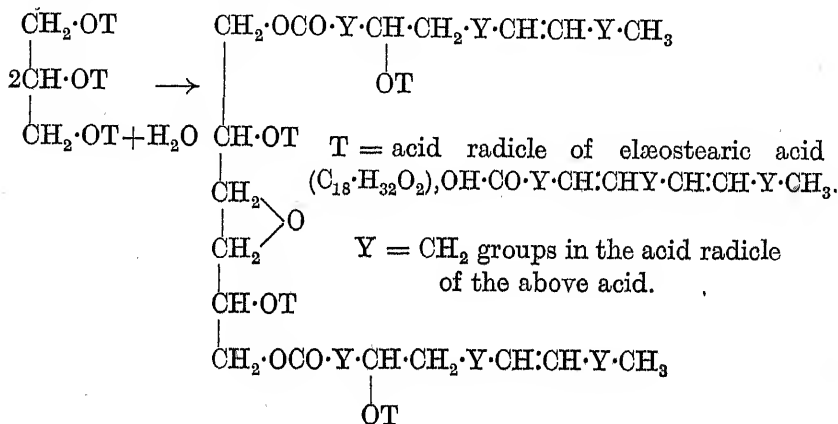
involving the formation of ring compounds which would tend to indicate stability of the products. Another representation has been

put forward by Staudinger ⁶ to explain the polymerisation of crotonic ester, and named by him condensed polymerisation :—

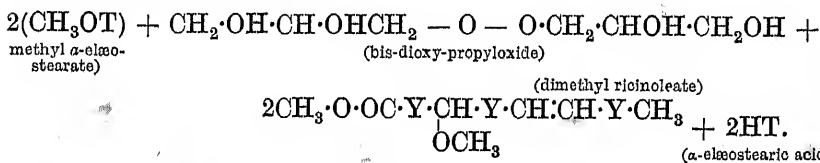


This representation would not be in keeping with the easy return of the polymerised substances to monomolecular conditions.

Salway's scheme as applied to thickened China wood oil seems to be more in keeping with facts.⁷



This, on treatment with sodium methylate and removal of the sodium, ought to give :—



It must be emphasised that the glyceryl radicle influences the thickening, although the ethyl and methyl esters will gelatinise, especially when heated *in vacuo*, but not easily.⁸ The identification of the two acids represented in Salway's scheme has not yet been carried out.

The application of the principles of colloid chemistry has caused other views to be put forward which may be instanced by a contribution from H. Wolff.⁹ The subject is discussed further from a colloid standpoint in Chapter VIII, p. 190. The changes in the properties of drying oils on heating are: (1) a greatly increased viscosity, (2) increase in density, (3) an appreciable diminution in

the iodine value, and (4) a considerable increase in the acid value in the case of linseed oil, but not with tung oil. The increase in viscosity and the fall in the iodine value do not take place concurrently, the increase in viscosity taking place chiefly after the iodine value has fallen to a steady value. The examination of the molecular weights as determined by the use of camphor¹⁰ as solvent showed values for stand oil varying between 1037 and 1430. Good values were obtained for the molecular weights of di- and tri-ricinoleic acids, but tetra- and penta-ricinoleic acids showed values 5—10 per cent. lower than those calculated from the acid values.¹¹ It cannot be said that the camphor method in molecular-weight determinations is superior to the use of solvents such as benzol or stearic acid for the oils, and glacial acetic acid for the oil acids. The results obtained by Wolff with the acids from thickened drying oils only confirm previously published work.

The tables on p. 161 show the variations in the iodine values with time and solvent, and the variation of the molecular weights with the solvent and concentration.

No definite conclusion can be drawn from Wolff's results that the phenomenon is a colloid gelation, in which at most only a small portion of the oil actually undergoes a chemical change, nor that the change is similar to the formation of a jelly by the addition of only 1 per cent. of gelatin to water. The conclusions of Wolff have been criticised by one of the authors, who has put forward views which are a compromise between the chemical and colloid standpoints. The influence of composition on the coagulation of drying-oil systems does not admit of interpretation from a mere consideration of variable degrees of dispersion or sizes of aggregates. It is possible that the so-called polymerised oils are instances of special molecular complexes of disperse material, which show apparent high molecular weights and low iodine values, permeated by medium which is of the same chemical composition.¹² The thickening of drying oils, especially China wood oil, appears to be a border-line case. There is no evidence of the occurrence of Staudinger's intramolecular polymerisation, because the acid obtained from the thickened oil is the same as that obtained from the unheated tung oil. As previously mentioned, the chemical changes outlined according to Salway's scheme have not been investigated, nevertheless an explanation by the formation of a dimeride is not fully applicable to account for gelatinisation. With regard to linseed oil, where the thickening requires prolonged heating, the possibilities of modification in the position of the ethenoid linkages are confirmed by inability

	Iodine Value (Wijs'.)	
Linseed oil (Baltic)	181.7 (1 hr.)	179.4 (16 hrs.)
Oleic acid	94.6 (1 hr.)	95.8 (18 hrs.)
Olive oil	92.0 (1½ hrs.)	86.7 (384 hrs.)
Linseed oil, thickened at 260° (insoluble in acetone)	121.4 (1½ hrs.)	136.0 (20 hrs.)
China wood oil, 3 hrs. at 205° :		
Insoluble in acetone	93.2 (2 hrs.)	150.8 (18 hrs.)
Soluble in acetone	151.5 (1 hr.)	160.5 (20 hrs.)
Acids from China wood oil thickened as above :		
From oil insoluble in acetone ...	126.5 (1 hr.)	140.0 (18 hrs.)
From oil soluble in acetone ...	137.7 (1 hr.)	143.6 (16 hrs.)
Thickened linseed oil, insoluble in acetone as above	{ 20 mins. in CCl ₄	99.7—115 (1½ hrs.)
	{ 23 hrs. in CCl ₄	123.2 (2 hrs.)
China wood oil, insoluble in acetone as above	{ 30 mins. in CCl ₄	76.85 (1 hr.)
	{ 23 hrs. in CCl ₄	107 (2 hrs.)

	Solvent.	% conc. of solution.	M. wt.	Calc. M. wt.	Investigator.
Oleic acid (iod. value = 96) ...	Benzol	2.836	545	282	Morrell (<i>J. Oil. & Colour Chem. Assoc.</i> , 1924, 7, 153)
Oleic acid	Glacial acetic acid	6.56	290	282	
Elaïdic acid	" "	6.67	297	282	
Acid from thickened linseed oil (insol. in acetone)	Benzol	6.5	1788	123.6	
Baltic oil (iod. val.)	Glacial acetic acid	6.23	388.2	—	
China wood oil ...	Benzol	6.45	805	—	Seaton & Sawyer (<i>J. Ind. Eng. Chem.</i> , 1916, 8, 490)
	Benzol	6.42	764	—	
	"	6.5	740	—	
Linseed oil	Benzol	5.55	803	—	
	"	0.59	930	—	
	Stearic acid	7.4	735	—	
Linseed oil acids from oil thickened 3 hrs. at 600° F. }	" "	3.8	740	—	
	Benzol	6.63	780	—	
	Stearic acid	5.1	335	—	

to identify linolenic or linolic acids from the depolymerised linseed oil. At any rate it must be admitted that the experimental results obtained from the ordinary methods employed to determine the degree of polymerisation are not of a strictly quantitative character. There is a tendency to connect the gelatin process with the formation of a dimeride, and perhaps this is the most satisfactory explanation at present, but such a compound is exceedingly sensitive to the influence of reagents, and is more of a molecular aggregation than a definite chemical compound.

Reference has been made under tung oil to the retardation of

gelation by the presence of small quantities of other substances. In general, increasing acidity retards thickening. Reduction of acidity by addition of small quantities of bases is found in practice to accelerate the thickening.

Comparisons of the water absorption and linoxyn content of drying oil films prepared from raw linseed and stand oil are given in the following table, as well as the gain in weight of the two drying oils on exposure to air :—

Water Absorption of Drying Oil Films after Treatment with Light Petroleum and Methylated Ether.

	Air-dried for	3 days' extraction with petroleum ether.	6 days' treatment with petroleum ether.	3½ days in methylated ether.	% linoxyn	Water absorption, %.			
						1 day.	2 days.	4 days.	8 days.
Linseed oil. (Pb and Mn driers.)	100 days	3.8% loss	Unchanged	35.3% loss	60.0	23.8	20.0	33.5	52.9
	30 days	—	—	00.5 02.4	30.5 37.0	—	Film white. After 3 days' immersion the film was white, 21.6 and 32.5. (3 days) 3.4, film white. (3 days) 15.2, film milky. (5 days) 23.0, film white.		
Lithographic oil. Pb and Mn driers	30 days	—	—	40.7	50.3	—			
Lithographic oil. Mn driers.	30 days	—	—	46.4	53.5	—			
Linseed oil. Pb and Mn driers.	12 hrs.	—	—	68.8	31.2	18.0 film cloudy			

It must be mentioned that the amount of polymerised oil present in an oil or varnish mixing must be carefully selected so as not to interfere with the smoothness of working and to prevent "drag." The presence of polymerised oil increases the quantity of thinners required to give suitable viscosity, with the result that, on application of the varnish, evaporation is more rapid and "shortness" may occur. It is not advisable in varnish mixings to replace the thin linseed oil by thick oil completely, because a year's exposure even indoors shows that the film containing thick oil only, replacing ordinary linseed oil, has developed cracks which are absent from a film with a thickened oil content of less than 50 per cent. In other respects, the films compared were alike in composition and in conditions of exposure. This is in agreement with A. H. Sabin's statement that stand oil is inferior to raw linseed oil in durability,¹³ but it must not be taken to show that addition of thickened linseed oil is a disadvantage, because experience has proved the advantages of its presence. This behaviour does not apply to other drying oils. A. Fibner and B. Wibeltz¹⁴ point out that the unsatisfactory nature of the films from poppy-seed oil as to softness, tendency to

crack and slowness of drying can be to some extent corrected by heating the oil in a stream of carbon dioxide for about 60 hours. Although the iodine value is much reduced by this treatment, the resulting oil dries much more rapidly and the film does not crack. Sunflower-seed oil cannot be improved by this means.

Comparison of Stand Oil with Linseed Oil.—The presence of thickened linseed and other thickened drying oils in paints and varnishes is considered to give coatings of greater durability and protection against corrosion. Friend, Toch and Ingle have each published results of exposure tests of paints on iron, and general experience confirms their results.¹⁵ The formation of any ring complexes consequent on polymerisation or of less unsaturated substances, according to the hypotheses of Staudinger and Salway, will retard the breaking down of the partially oxidised glycerides to give volatile aldehydes produced by the disruption of a double linkage subsequent to oxidation; this may be illustrated in the case of China wood oil, which on partial drying rancidifies with the formation of volatile aldehydes. The oxidation of tung oil in the presence of metals has been shown to proceed in two stages, indicating a difference in the activity of the unsaturated grouping. Whether the groupings where union may be presumed to occur during the thickening by heat are the same as where oxygen is absorbed on drying, it is not possible to decide. The drying process of the thick oil proceeds on the same lines as in the raw oils as regards the formation of peroxides. It is in the stability of the peroxides of the thickened oil that an explanation of the durability must be looked for. Increase in the number of ethenoid linkages in a drying oil is not always conducive to durability of the oxidised film. Reference has already been made in this respect to the properties of fish oils and China wood oil.

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31, 109, 121. ¹⁵ M. Toch, *J.*, 1915, 34, 592; H. Ingle, *ibid.*, 1919, 38,
102; J. N. Friend, *J. Oil and Colour Chem. Assoc.*, 1922, 5, 263.

CHAPTER VII

THE USES OF DRYING OILS IN OTHER INDUSTRIES

(a) LINOLEUM AND FLOORCLOTH

LINOLEUM and floorcloth differ from paints and varnishes in the function of serving primarily as mechanical insulators and decorative coatings, and not as protective agents against decay and corrosion.* The employment of linoleum has of recent years assumed gigantic proportions, and on account of its hygienic properties it is a popular substitute for carpets, especially in public buildings, shops, etc.

The discovery of linoleum dates from about 1862, and had its origin in the curiosity and enterprise of Frederick Walton (Walton, Taylor & Co., Staines), who, while searching for a cheap substitute for rubber, noticed that the skin of the oil from a can of paint was tough, elastic and rubber-like. He conceived the idea that the peculiar properties of this material could be used for some practical purpose. In 1844, Elijah Galloway took out a patent for the manufacture of a cement of indiarubber, plasticised by steam and mixed with powdered cork to give a mass which, when rolled to the desired thickness between smooth cast-iron rollers, was known as Kamptulicon. In 1864, Wood produced a fabric of pulped bullock hides and hair, coated with oil varnish or oil paint, which was known as Boulmikon and was of good durability.

Linoleum has for its principal ingredients oxidised linseed oil, resins, pigments, wood or cork flour. From the first it receives its excellent wearing qualities, while from the last two it acquires resiliency as well as general insulating properties. It is mounted on a canvas backing "burlap," having a width of 6—12 feet, a warp and weft of equal strength and of uniform mesh, which serve as a foundation or back for the cement and fillers. It is usually painted red on the underside, as a protection from water and other injurious materials with which it may come in contact. It appears in three forms, "plain," i.e., uncoloured; "printed," in which a superimposed painted design has been impressed on a plain linoleum, and "inlaid," in which a carpet pattern extends right through from the upper surface of the canvas. The body of the material can be detached as a whole from the canvas.

Floorcloth.—Floorcloth is of older origin than linoleum, and the first patent of the material was taken out by Nathan Smith of London in 1763. It was then composed of rosin, pitch and Spanish brown in equal quantities, with the addition of beeswax and linseed oil, the quantity of which was varied according to the season of the

* Linoleum is stated to possess extraordinary power as a germicide.

year. The mixture was applied to the canvas in a melted state and rolled in by pressure from a heated hollow iron roller. The oldest surviving firm in the trade in England is J. Hare and Co., Bristol, who advertised floorcloth manufacture in 1788.

M. Nairn, of Kirkcaldy, established floorcloth works in 1847. The demand for floorcloth has been largely superseded by linoleum, and it is advisable to refer only briefly to what is almost a declining industry. The canvas used in the manufacture is chiefly jute. The oilcloth or floorcloth is produced by painting both sides of the canvas foundation with layers of oil paint, and finishing by printing a pattern in one or more colours on the final layer. There are two qualities, heavy or hand-made (25 yards long and 8 yards wide) and a light or machine-made product (12 feet wide and $3\frac{1}{2}$ lb. weight per square yard, against 7—8 lb. in the hand-made quality).

In hand-made floorcloth, paint is applied to the canvas held in wooden frames in a vertical position. At first a dilute solution of size is applied, followed by a stiff ground of oil paint applied back and front like plaster. The paint is composed of linseed oil, linseed oil foots, varnish bottoms, whiting, China clay and earth oxides, the mass being reduced to a working consistency with white or shale spirit. After 10 days' air-drying the coating is rubbed down with pumice and a second coat of stiff paint is applied, followed by a third coat after another 10 days' interval. The facing surface receives two coats of paint, applied by a brush and not by a trowel, as are the previous three coats. On the facing surface a printed pattern is applied by means of wooden blocks, a separate block being necessary for each colour of which the final pattern is composed. The printed floorcloth requires to be matured for 8 or 9 months. A lower grade of floorcloth is produced entirely by machine application. The layers of paint are fewer and are applied by a trowelling machine, the final pattern being printed by rollers, one for each colour, with the pattern in relief, as in the case of blocks. Usually four coats are applied on the facing-surface, with two on the back. The rubbing down is also done by revolving pumice-stone rollers. The printing machine consists of a large revolving iron drum, against which are pressed the rollers to which the colours are fed by means of hollow iron cylinders covered with gelatin and revolving in a trough of paint. The floorcloth to be painted passes between the iron drum and the printing rollers, and the points where they impinge are where the colour of the pattern is transferred to the fabric. Each roller prints only one colour and

one portion of the design, and there are as many rollers required as there are colours in the pattern.

The printing of floorcloth is now more commonly done on the horizontal machine used in connection with the printing of linoleum.

The printing rollers consist of an iron core surrounded with wood, thickly coated with gelatin, and this is cut away to leave a pattern in relief. When the design requires a deposit of colour in a mass, rollers of this type alone are used, but in tessellated or mosaic designs or in parquet, in which the design of the wood is imitated, and also in fine matting effects, brass or copper strips or wire are inserted into the wood to obtain the fine details, which would be impossible with gelatin- or composition-covered rollers. Hand-made floorcloth possesses the advantage over the machine-made variety of being capable of manufacture in greater widths. Floorcloth possesses neither the wearing properties, resiliency nor heat- and sound-proof qualities of linoleum.

Linoleum.

The two principal ingredients of linoleum are linseed oil or a drying oil, incorporated with a resin and cork or wood fibre. From the drying oils it receives its wearing qualities, and the oils with the resin act as a binding medium. Resiliency, sound and heat-insulating properties are obtained from cork and wood fibre or wood flour. Resins and pigments play important parts in the structure of the linoleum material. The linseed oil must be made into a cement, the pigment into a paint, and the cork dust and wood flour refined and ground to the proper size for use.

Scrim Process.—The oil oxidation processes command attention for their contrast with paints and varnishes. The methods of manufacture are two in number, and no radical changes have been made since the time of the inventor sixty years ago.¹ In the first and oldest method, the "scrim" process, raw linseed oil is heated for 4—8 hours to 350—500° F. by a direct fire in large iron pots each with a capacity of 240 gallons, fitted with a slow-running agitator, in the presence of metallic driers, 2 per cent. litharge or, preferably, 5—10 per cent. lead acetate, and plenty of air, until the proper body is obtained. It is then pumped into storage tanks, where, after cooling, it is transferred in smaller movable conveyors to the top of the oxidising shed, which is a heated building 24—30 feet high and large enough to accommodate from 200 to 3000 cotton "scrim" cloths, each about 3 feet wide by 25 feet long, hanging

from the ceiling in close formation. The process consists in forcing the oil through perforations of $\frac{1}{80}$ inch diameter in the bottom of the trough on to the "scrim," and allowing the film of oil to undergo oxidation on the cotton fibre, the solid oxidised surfaces being employed as undercoats for subsequent layers, until thicknesses of $\frac{3}{4}$ —1 inch are obtained. The oil from the conveyor is allowed to trickle or spray over the cotton sheets, while the excess oil dripping from the cloths is allowed to run back into the storage tanks. F. Fritz² states that this oil consists essentially of saturated glycerides, indicating a rearrangement of the mixed glycerides during the oxidation, which is not observed in the oxidation of linseed oil at the ordinary temperature. The air is kept at 100° F. and, after

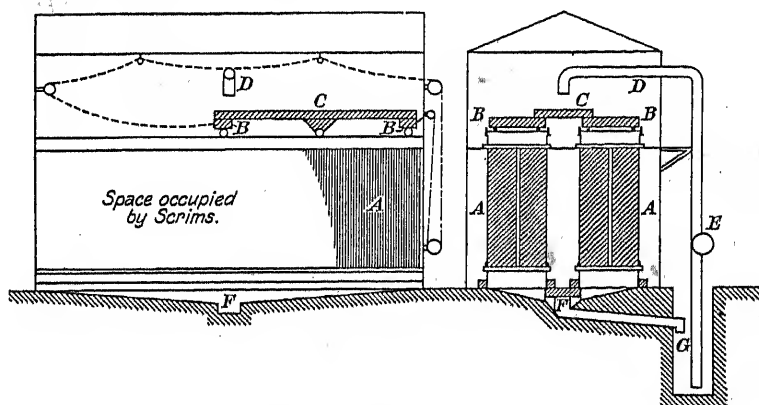


FIG. 18.—Diagrammatic Representation of Scrim Plant.

A. Scrim in Rack. B. Flooding Troughs. C. Distributing Trough.
D. Oil Pipe. E. Pump.

several hours, the oil on the "scrim" solidifies to a tough elastic film. The flooding of the cotton sheets takes place twice daily for 3 months, and the oil will show a gain in weight of 5—8 per cent., due to oxygen absorption. The heavy "skins" are torn from the hanger and piled in a storage house until required for use in linoleum cement. Another set of "scrim" is then started in the same shed (see Fig. 18). The oxidised oil at this stage may be lightly ground through iron rollers, to give a powdery substance, which is spontaneously inflammable on exposure, and it must be immediately incorporated with resins and kauri, in the proportion of 30 per cent. of the weight of the oxidised oil used, in steam-jacketed pans.

After a time, the heat causes the mixture to become fluid, and, when a suitable consistency is reached, the pan is tipped up and its contents allowed to cover a prepared floor, to a depth of about 6

inches. When cool the mass is cut up into small blocks and is now known as cement, which is to be mixed later with cork (cf. p. 170).

Walton Shower-bath Process.—In the shower-bath or mechanical oil process, the oil, which has been previously heated to 50° with metallic driers (manganese borate in suspension) is pumped to the perforated ceiling of a large heated room, where it drips through the perforations to the floor below in the form of rain. A fan serves to change the air in the oxidising chamber and to remove volatile products. The circulation is maintained until the viscosity has increased to the consistency of heavy molasses and the oil will not pass through the perforations of the roof. The time required varies from 24 hours to 6 days, depending on the temperature, the

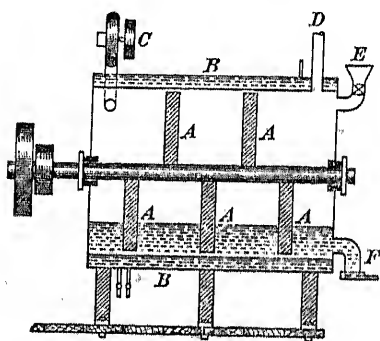


FIG. 19.—Diagrammatic Representation of Walton's "Smacker."

- | | |
|----------------------|-------------------------|
| A. Beaters. | B. Water Jacket. |
| C. Air-inlet Fan. | D. Air-outlet Pipe. |
| E. Oil Charge Valve. | F. Oil Discharge Valve. |

humidity of the air drawn in, and the driers employed. The continuation of the oxidation is proceeded with in another apparatus known as a "smacker." The "smacker" consists of a horizontal jacketed drum, of a capacity of about 400 gallons, fitted internally with rotatory radial arms. The thick oil is run into the "smacker," and the stirring gear started. Steam is passed into the jacket until the temperature of the oil reaches 130° F., and common whiting is added to the charge to the amount of 5—6 per cent.

of the oil. A device for circulating fresh air is fitted into the "smacker." Once started, oxidation in the "smacker" proceeds so rapidly that the steam is shut off from the jacket and cold water passed in, so that the temperature may not rise above 120° F. Test cocks at the bottom of the "smacker" allow samples to be withdrawn at intervals. In about 20—40 hours the oil attains such a degree of oxidation that, on cooling, it will set to a pale, rancid-smelling oil of about the consistency of common strong size. The "smacked" oil also possesses a slightly honeycombed structure and is almost devoid of greasiness. The honeycombed structure is further developed, and the last traces of greasiness are removed, by warming up to 160° F., in steam-heated ovens, for several days. The use of the whiting may be to produce carbon dioxide by neutralisation, causing the honeycombed structure, or to remove greasiness and to assist in thickening of the oil by polymerisation (see Fig. 19).

Some manufacturers prefer to simplify the process by pumping the raw oil, with driers, directly into the retort or "smacker." In this modification 15—60 hours are required to complete the process. This method, carefully handled, with proper driers at correct temperatures, furnishes a highly satisfactory mechanical oil, applicable for use in all grades of linoleum. An oil heated at a low temperature, with a small amount of drier, will require a longer time for complete oxidation than an oil heated at a higher temperature. On the other hand, the former will produce a more satisfactory grade of cement. A careful and exact control of the complete process must be exercised.

It is considered by some authorities that the scrim process produces a more uniform quality of oxidised oil than the "smacker" process. "Scrim" oil is the result of an average mixture of deliveries of linseed oil during four or five months, with iodine values ranging from 175 to 190, whereas "smacker" oil uses up the deliveries as they come in, thereby saving expense of storage.

Taylor Oil.—Another important binding material used, especially in the manufacture of cork carpet (corticene), and to a lesser degree in plain and printed linoleums, is Taylor oil, which was patented in 1871.³ It is prepared by boiling raw linseed oil (2—3 tons) with driers (2—3 per cent. of litharge or 1 per cent. of litharge with 1 per cent. of lead acetate, the function of the latter being to redissolve any metallic lead resulting from the reduction of the litharge). The oil is heated to 300° F. and, as soon as the driers are dissolved, a long iron pipe, reaching to the bottom of the pot, is fitted and a vigorous current of air is forced through the oil for 2—3 days, to maintain a constant temperature (300° F.) and to supply the oxygen necessary in the operation. The liquid gradually darkens, finally assuming a reddish hue and possessing an unpleasant acrid odour. When this stage is completed the oil is transferred to smaller pots, holding 12—15 cwt., and heated by fire as before. In these the temperature is raised to 450—500° F., and a rapid reaction takes place, which must be kept under control by drawing the fire, or by other methods, as experience dictates. After 6 or 7 hours' heating, when signs of incipient solidification are noticed, the oil is well stirred and the fire withdrawn. Complete solidification takes place somewhat rapidly, and as it proceeds throughout the pot, disengagement of gas within the mass results in the contents rising so high that a series of short cylindrical rings have to be placed round the upper edge of the pot, to retain the contents as they rise. Rising to a loaf-like head ensues and continues for several hours, after which a slight contraction occurs.

After the reaction has subsided, the temperature is raised to 600° F., at which it is maintained for some hours, until a sample shows signs of becoming stringy when cooled. The pot may be lifted by suitable gear, and its contents tipped into a prepared bay on the floor, and before the mass is quite cold, it is cut into blocks and stored away. The resulting product is dark in colour and resembles soft and unvulcanised spongy rubber. This oil is considered to be a polymerised product, owing to the high temperature during its manufacture, although containing a portion of oxidised oil. Therefore it may be distinguished from those already described under the head of oxidised oils prepared at low temperatures. The solid oil has a honeycombed structure in the centre, whilst the bottoms and sides are sticky. After thorough amalgamation of the sticky bottoms, dry middles and tops, through mixing rollers, the oil is ready for direct use as a cement, without any further treatment. Taylor oil, while not so suitable as a binding medium for linoleum, is an ideal cement for cork carpet and for similar products which require resilient properties.

Neither "scrim" oil nor "smacked" oil possesses the required physical properties to permit of their being used as a binding medium. They are elastic, but lack the binding power necessary to hold together the other ingredients, viz., cork dust, wood flour and pigment. It is essential to obtain a product with properties similar to unvulcanised rubber in its warm, tacky stage.

Linoleum Cement.—Linoleum cement is prepared as follows: The ground "scrim" oil pulp and solid "smacked" oil are fluxed with melted rosin, in a large vertical steam-jacketed kettle provided with an agitator. When these ingredients are thoroughly fused and blended together, powdered kauri gum is added, and the whole mass is gradually heated to about 275° F., when, after a few hours of constant stirring, it thickens into a dark-coloured plastic material known as linoleum cement. Another form of cement plant consists of a steam-jacketed pan, with a capacity of 200—400 gallons, fitted with a vertical or horizontal stirring gear and a sluice valve at the bottom. At the top of the pan is a charging hole about 1 foot in diameter. In the case of the shower-bath process, the "smacked" oil is added in large pieces, whilst in the "scrim" process the skins are ground to a meal, through steel rollers, in order to disintegrate the contained cotton fabric. Steam is passed into the jacket, and when the oil begins to fuse, melted common rosin (12 per cent. of the weight of the oil) is added, followed by a similar amount of kauri gum dust. Excessive effervescence is checked by increasing

the speed of the stirrers at the proper moment, as both under- and over-cementing are fatal to the production of a successful cement. A prompt arrest of the reaction is facilitated by either tipping the contents of the cement pan on to the apex of a mound on a concrete floor, or preferably by discharging the contents into a hopper, leading to water-cooled rollers, and thence into separate trays, where cooling takes place comparatively rapidly. The cement when cold is very tough, rubbery and elastic, and when properly made should be of a stringy nature when pressed between the fingers. The consistency of the cement is of great importance, hence each batch is tested physically before being worked up into linoleum. The manufacture of the cement resembles that of varnish without thinners, except that the oil used has been previously partially oxidised.

The difference between linoleum and corticine is, broadly speaking, that the oxidised oil used in the former is made by one or other of the Walton patents, whereas that used in the latter is prepared by the Taylor process. Both products have equal merit, but differ in slight details. In linoleum, fine-grained cork is used and a certain amount of wood flour is added. The crude cork is obtained from Spain, Portugal and Algeria, and after being thoroughly dried, it is passed through a form of disintegrator in which, by means of saw-toothed rollers, running at different speeds, the lumps are torn apart into pieces of the size of peas or filberts. It is then passed through flat millstone grinding mills, about 4—5½ feet in diameter, which deliver the cork as fine powder. The cork is next sifted through revolving sieves of wire gauze, 20—60 meshes to the inch, according to the fineness desired. The crude cork must be carefully picked over to remove anything likely to produce a spark by friction, as the powdering process produces much dust, and care has to be taken to prevent explosions and fire.

There are three classes of linoleum: plain or single-coloured floor covering; printed linoleum, which is simply a thin grade of plain linoleum, on the surface of which has been printed a coating of oil paint; inlaid linoleum, distinguished from printed linoleum by the fact that the coloured designs or patterns extend completely through to the canvas back.

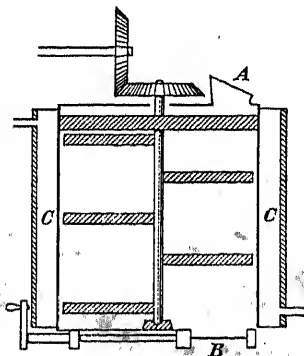


FIG. 20.—Diagrammatic Representation of a Cement Pan.

- A. Charging Hole.
- B. Discharging Valve.
- C. Steam Jacket.

Plain Linoleum.—This variety demands the simplest treatment and represents, in its method of manufacture, the preliminary stage in the production of all the varieties. The ingredients are a mixture of ground cork, pigment and linoleum cement. The amalgamation is carried out in horizontal mixers, similar to bread-kneading machines, and the ingredients are intimately mixed to produce a plastic mass or dough. From here the mixture is passed into a steam-heated machine, resembling a large meat-grinder, where the cement and fillers are thoroughly blended together. Emerging from this operation in the form of shreds, the mix is run over scratch rollers, to form a coarse granulated powder, which is then spread evenly over a moving strip of canvas and the whole passed between the heavy steam-heated rollers of a calender. The powdered mass is firmly pressed into an even coating on the canvas back. The canvas backing is coated with a layer of cheap yellow ochre or red oxide paint, which is spread as evenly as possible by a trowelling machine. The composition of the paint is such that it requires melting in a steam-heated pan previous to application, and it solidifies on cooling to a non-tacky coating on the canvas. The final process consists in maturing the "green" cloth in large stoves, about 65 feet in depth, in the form of loops or folds, at a temperature of 140—160° F. The time required for the linoleum to mature varies from 1 to 8 weeks, depending on the thickness and construction of the linoleum fabric. When it is deemed to be of sufficient hardness to withstand wearing, and will resist a standard indentation pressure, the material is trimmed so that the cloth is of standard width.

Printed Linoleum.—In printed linoleum the "green" cloth is painted on its face by either machine or hand. The large horizontal printing machine, which applies the surface paint by means of printing blocks, is usually equipped to print 1—10 different colours and designs in one operation, although 24 colours can be used by a modern printing machine. The movable printing blocks resemble the ordinary engraving plate, and are usually about 18 inches wide and 6—12 feet long, corresponding to the width of the linoleum. While the blocks are automatically raised to take a coat of paint, the strip of linoleum moves forward just the width of one block, so that, with each downward movement of the block, a finished strip of linoleum 18 inches wide is obtained. As the printed material leaves the printing machine it is transferred back into the drying oven for several days, until the paint is perfectly dry. In hand-printing it is the practice to apply successively the different colours forming the pattern in the portion of the cloth under printing treatment.

Inlaid Linoleum.—However satisfactory a newly-printed piece of linoleum may appear, the pattern will not last as long as the bulk of the fabric, and to remedy this defect many processes have been suggested. These ultimately merge into what is known as inlaid linoleum, in which both colour and pattern go through from the surface to the canvas backing. As early as 1863 F. Walton took out a patent in this direction, and in 1882 he devised machinery for mosaic floorcloth and eventually perfected a machine for making inlaid linoleum at a rapid rate. In the manufacture of inlaid linoleum wood flour is substituted for part of the ground cork, in order to give a firm and dense linoleum mixture necessary in building up the pattern. There are two classes of inlaid linoleum: granulated or moulded, and straight line, depending upon the method of manufacture.

Moulded Linoleum.—In the case of the moulded variety, the linoleum mixture is applied on strongly greased paper or on a canvas back in a granulated form by means of metal stencils. A grid, cast to a pattern corresponding to the design required, is laid on a table in a horizontal position, successive stencil plates having openings corresponding to sections in the grid being placed on the top, and the meal of a particular colour chosen to fill these sections is dusted in. For a three-colour pattern three stencil plates will be required. The pattern having been arranged on a sheet of strong greased paper, the stencil is removed, the grid carefully lifted so as not to disturb the loose "meal," and the paper support with its layer of "meal" pulled along under a hydraulic press, the upper surface receiving a section of the run of canvas destined for its final support. It will be seen that this linoleum is built up from the back, although the granulated linoleum material may be fed directly upon the canvas, each colour through its own particular stencil. The moving canvas passes through a large heated hydraulic press where a pressure of 2000 lb. to the sq. inch fuses the mass to the back. At the same time, all the granular particles of the different colours have disappeared into one smooth surface of linoleum fabric. It is then taken into the drying stove, where it is laid horizontally, as it will not stand the bending necessary in hanging from battens as in the drying of ordinary linoleum. The machinery for this process was the subject of a patent granted to Godfrey, Leake and Lucas (1888).

Straight-line Inlaid Linoleum.—This is easily recognised by the clear straight-edged line separating the different designs, which in the case of moulded inlaid is of a ragged nature where the grid has been dispensed with and the building up has been carried

out from the canvas face instead of from the back. The machine, which is very massive, is too complicated to describe here, but its essential features consist in cutting out, from sheets of differently coloured linoleum, up to six in number, the pieces required to form the desired pattern, with the fitting together of these separate units upon the canvas backing, and by means of heat and pressure uniting the whole into one perfect piece, the operations being continuous and automatic. In certain of the patterns turned out by this machine some of the separate pieces are so small that 16 of them only cover 1 sq. inch. In one day over 90 millions of these units are separately cut out and placed with unerring accuracy in their proper positions in the design. In these newer Walton inlaid, characterised by clearness of outline and cohesion of the finished product, the oil must be made by the "shower-bath" process, owing to the greater cohesion required in the intermediate stages of manufacture.

The proportions of ingredients employed in the manufacture of the different varieties of linoleum are trade secrets. The following figures, taken from F. Fritz's communication,⁴ will give some idea of the proportions used: plain linoleum, 25 kg. cork meal, 20 kg. cement, 10 kg. ochre or other colours; granite linoleum, 25 kg. wood flour, 20 kg. cement, 8—12 kg. colour; inlaid linoleum, 25 kg. wood meal, 23—25 kg. cement, 8—15 kg. colour; corticine, 25 kg. wood flour, 15 kg. black oil, 3.5 kg. ochre or other colours. It is evident that the quality of the products depends on manufacturing conditions more than on the differences of the quantities of the ingredients.

From the description of the processes it is clear that it is highly desirable to reduce the time taken in the oxidation of the oil and the maturing of the product. The importance of this is indicated by Fritz,⁴ who points out the serious drawbacks of the "scrim" process. It is necessary to wait for 120 days until a "scrim" house can be cleared. It is true that the one daily application of the oil, at 38°, has been increased to two applications at 42°. There is the loss of the "scrim" cloth, which is left in the linoleum, and forms 0.74 per cent. of the weight of the linoxyn. Fritz has also recommended the use of a glycerin glue-coated fabric, so that the linoxyn may be easily removed from it and the fabric can be used again.⁵ The expense of heating the oxidation house is a serious charge on the industry, in view of the large size of the building in which the linoleum undergoes treatment in the various stages; moreover the time of oxidation and the temperature can be reduced

by suitable modifications of the driers. The customary 2 per cent. litharge drier can be replaced by a mixture of driers giving 0.5 per cent. Pb and 0.1 per cent. Mn, or by 0.66 per cent. Pb and 0.13 per cent. Mn on the oil.⁶ G. F. Holden and L. G. Ratcliffe⁷ consider that the time of oxidation can be reduced from 4 months to a few hours and the temperature reduced from 42° to 20°. The higher the temperature of oxidation of the oil the less the increase in weight in the drying of the linoxyn, because of the greater loss of volatile products. The presence of too much manganese makes the inlaid linoleum too hard. Too strongly dried linoxyn can be reduced by the addition of stand oil during the cement process. The introduction of oils other than linseed has been considered, especially China wood oil. The difficulties in the rapid polymerisation of wood oil by heat require to be overcome by the use of comparatively large quantities of resins, which make the cement brittle. It is not advisable to add larger quantities than 10 per cent. of wood oil mixed with linseed oil in the "scrim" process. The use of cobalt driers is worthy of consideration.

From a practical view-point, the chemical changes which occur during the preparation of linseed oil for use in linoleum manufacture are divided into two classes, oxidation and polymerisation or gelatinisation. Under the former are included the "scrim" and mechanical oils, while under the latter are included linoleum cement and Taylor oil, although there is still some discussion as to whether linoleum cement is a true polymerised product.

The reactions taking place in the maturing process of linoleum fabric must be largely due to completion of the oxidation and of the gelatinisation, the former of which is dependent to a great extent upon light, temperature, moisture and the driers used in the oil. The higher the temperature of oxidation, the smaller the increase in weight, due to the formation of volatile oxidation products. Instead of a normal increase of 16 per cent. in the weight of the linseed oil, the increase is only 6—8 per cent., due to losses in the oxidation and cementing processes. The presence of surface driers in excess will retard the proper course of the oxidation. The complete action, especially in heavy plain linoleum, has been known to continue over a period of years, due to the fact that an almost impervious film forms over the surface of the linoleum, preventing the oxygen in the air from coming in contact with the unoxidised portion of the oil. The proper degree of oxidation in the various stages is determined by the manufacturer, as it is so dependent on his special conditions. The general choice of lead as the chief drier

confirms the experience of the varnish-maker, who prefers it for linseed oil. With proper oxidation and maturing, there is no sweating of the finished surface, as might be expected if the oil were superoxidised, as was observed by Reid⁸ (this observation of Reid's has not been generally confirmed as being the result of over-oxidation, but is looked upon as gradual degelatinisation). In linoleum there are to be found defects resembling those in enamels containing resins, and the factors which govern the production of a good linoleum are to be looked for in the conditions for the production of a tough, hard, uniform gel. These factors are at present not satisfactorily understood in the case of varnishes, and in the more complex linoleum the secrets of successful production remain with the craftsman. (Cf. *The Industrial Chemist*, 1925, 1, 377),

(b) DRYING OILS AS ELECTRICAL INSULATORS

A. Bartoli, after an examination of the electric conductivity of oils and fats, concluded that (a) the conductivity increased with rise in temperature and varied with the nature of the oil, (b) drying oils when exposed to the air acquired a greater conductivity than non-drying oils. An increase in conductivity to a smaller extent was shown in non-drying oils when they had become rancid. The more unsaturated the oil the greater the conductivity when exposed to air, so that olive oil showed a lower conductivity than linseed oil.

It is evident that acid decomposition products from drying oils increase the conductivity. In the presence of driers and resins, oxidised linseed oil is classed among dielectrics, together with asphalt and bitumen, stearine-pitch, paraffin, shellac, and natural and artificial resins. A discussion on the application of these substances involves a study of the properties of insulating materials, including oil and spirit varnishes. A dielectric is a type or condition of matter or space in which it is possible to produce and maintain a continuous state of electric stress with little or no supply of energy from outside sources. Non-conductors are often termed dielectrics when their particular function is to separate neighbouring conductors which are at different potentials. Dielectrics may be solid, liquid or gaseous. The distinction between a dielectric and a conductor is that in the space between two conductors separated by a dielectric, a state of electric stress can exist without the continuous supply of energy from outside the system, whereas in the case of a conductor an appreciable and often very large amount of energy is required to maintain the same condition. There is no hard-and-fast line between conductors and dielectrics. Probably all dielectrics allow

a very minute current to pass through them. Many materials which are efficient dielectrics at ordinary temperatures gradually alter as the temperature is raised and become conductors (Curtis, *Bull. Bureau of Standards*, 11, 371). This property is common to a number of substances of mineral nature, *e.g.*, glass, porcelain and metallic oxides, as in the Nernst lamp. At about 2000° or less all insulating materials cease to exist. The following values are given of the specific inductive capacity of a number of insulating materials: ebonite, 2.7—2.9; glass (crown), 5—7; glass (flint), 7—10; india-rubber, 2.1—2.3; dry paper, 2—2.5; pitch, 1.8; mica, 5—7.7; shellac, 3—3.7; resins, 1.8—2.6; bakelite, 5.7—6.8; paraffin, 4.6—4.8; castor oil, 4.6—4.8; olive oil, 3.1—3.2; turpentine, 2.2—2.3; petrol, 2—2.2; air = 1.*

Applications of Dielectrics.—These act as mechanical separators of conductors at low voltages, such as in dry-core telephone cables, where pressure does not exceed 30 volts, each wire being spirally wrapped with paper ribbon and air dried. In submarine telephones and telegraphs, the insulating material is gutta-percha, chosen for its toughness, flexibility and resistance to sea water. For domestic electric circuits indiarubber protected by braiding which is treated with a wax preparation issued.

In insulation for moderate voltages up to 500 volts, paper and woven fabrics require waterproofing with insulating material, which may be either shellac, oxidised linseed oil and varnishes, or bituminous varnishes and synthetic resins.

In insulation for high voltages, as in transformers and in transmission cables, the insulation consists of paper saturated with highly-refined mineral oil.¹⁰ According to Fleming and Johnson,¹¹ the varnishes can be classified into: (a) varnishes for impregnating windings, (b) varnishes for treating papers and fabrics, (c) varnishes for cementing purposes, (d) finishing varnishes. Each of these classifications can be divided into air-drying and stoving coatings. The varnishes of classes *a* and *b* must be capable of withstanding oil and moisture and high temperatures, and other special properties are called for when classes *c* and *d* are specified. The drying oils are components of classes *a* and *b*. The linseed oil may also be incorporated with a resin or an asphaltum. The coatings possess high dielectric strength and are, when thoroughly oxidised, very nearly impervious to moisture and oil. They contain vegetable

* While the sp. resistance and the sp. ind. capacity of materials are guides to their insulating value, the method of application and conditions of use must be considered.

acids, but as a rule the corrosive effect is neither serious nor lasting. In the stoving of these coatings the volatile solvent is first expelled and the oxidation of the oil and gum proceeds, assisted by a small amount of a mineral drier, preferably manganese or cobalt. The formation of a solid film renders the complete oxidation of the oil a slow process, so that flexibility is retained for a long time. The tendency of short oil varnishes is to become brittle in time, so that perhaps for that reason it may be considered that the longer the varnishes take to dry the more permanent they will be as insulators.

Insulating varnishes must be carefully checked and tested in the laboratory, because a predetermination of their expected behaviour will allow of economy of time and material and prevent interruption of the usual factory routine. The following characteristics must be examined: penetrating power of the fluid varnish; viscosity and density; the flexibility and durability of the dried varnish at high temperatures and in moist atmospheres, as well as the heat insulation and resistance to the action of chemicals (acids, alkalis and solvents, *e.g.*, petrol, benzene and mineral oils). The air-drying and stoving properties are also of the highest importance. The determination of the dielectric strength, the break-down voltage and electrical resistance is a matter for the electrical engineer, but the chemist is able to appreciate the significance of the figures obtained, and to correlate them with chemical and physical characteristics, so as to specify the most suitable material for the particular object in view.¹²

The direct application of drying oils is in the form of impregnators of fibres and windings and as tapes for insular-joints and awkwardly-shaped coils, where sheet insulators cannot be applied directly, and for treated papers used in insulation of transformers, especially oil-cooled types. The requirements are high dielectric strength, flexibility, permanence, non-absorption of water, and resistance to the action of hot oil.

One of the best known of the treated fabrics is Empire Cloth and a number of similar materials sold under trade names. These materials are prepared by impregnating cambric with linseed oil or linseed oil-resin-varnish and drying thoroughly. The cambric acts as a support for the varnish, and long strips, about 4 feet wide, are passed through a varnish vat and dried in an oven at temperatures up to 100° for 8—10 hours. The material varies from 0.005 to 0.015 inch in thickness and has a smooth surface. The dielectric strength and the flexibility of material depend on the varnish, but the durability and ultimate value as an insulating medium depend on the cambric, which should be closely woven, undressed, without nap and about 0.004 inch thick. A 4-mil. cambric will

give a 6-mil. thickness with one impregnation and about 9 mils. with a double coating of varnish. All fabrics tear and are liable to split very much more easily after being treated. It must be pointed out that before impregnation the fabrics should be dried. This tends to reduce the flexibility, but unless moisture in the fibre has been withdrawn, the dielectric strength, especially when the insulation is heated, will be seriously reduced.

The tapes are not very elastic and do not lie well on irregular surfaces, and although improvement may be made by cutting the tape, so that the threads run diagonally across the strip, yet too much tension cannot be applied, because the fabric will stretch more than the varnish film, causing the latter to break, thus reducing the dielectric strength. The importance of thoroughly oxidising the linseed oil to the linoxyn condition must not be overlooked and prolonged stoving is essential. Although the permeability of an oxidised oil film is low, its water-absorbing property may be high, especially if it contains enclosed unoxidised oil. The unoxidised oil is apt to form an emulsion with the penetrating water, causing the film to become soft and to undergo strain through swelling, which in some cases may be so great that the outer film is ruptured. In a breakdown test, the tape may be wrapped round a metal rod about 1 inch in diameter, overlapping each turn one-half the width of the tape, and the breakdown voltage determined. The tests are to be repeated at intervals of 24 hours after exposing the test piece to a temperature of 100° in a well-ventilated heater, and the ageing continued for 10 days. The general tests, in addition, would include mechanical strength tests: (a) on the product in its original state, (b) on the cloth which has been slightly heated, (c) on cloth which has been dipped in hot oil (transformer). Details of the method of testing will be found in A. R. Matthis, "Insulating Varnishes in Electro-Technics," and A. P. M. Fleming and R. Johnson, "Insulation and Design of Electrical Windings."

Most electrical engineers have their own special methods, but in general the principles are the same.

The methods of applying varnishes comprise, first, the drying of the material to expel all humidity before impregnation by dipping with the oil or oil varnish. The drying can be carried out in an ordinary oven at a temperature between 100° and 110° . It must be remembered that the materials to be dried are extremely hygroscopic, so that they will reabsorb moisture during any interruption of the drying. Continuous heating is therefore necessary. Vacuum drying is the most economical system, as it is the most rapid and can be carried out at comparatively low temperatures, because the

boiling point of water is about 35° when the vacuum is 735—745 mm. Immediately after drying the pieces should be immersed in the tanks which contain the varnish chosen. Immediate immersion in the varnish after drying the material will cause a thickening owing to the increased evaporation of the solvent, so that from time to time the varnish will have to be brought back to its proper consistency by the addition of thinners. Air-drying varnish is used for impregnation when the pieces are too large to go into the oven or baking facilities are lacking. The objects impregnated in baking varnish should be allowed to drain so as to reduce the waste of varnish to a minimum, and the tanks must be large enough to prevent the temperature of the pieces which are dipped having any effect on the temperature of the varnish, thereby causing undue evaporation of the solvent, so that uniform impregnation will be interfered with. In the oxidising ovens evaporation of the solvent and oxidation of the varnish proceed simultaneously, and the form of the stove and its heating demand careful attention. As to the source of heat, gas, steam, or electrical heating may be employed.

The necessary draught to ensure adequate oxidation must be carefully controlled and the distribution of heat in the stove is essential; whether large or small ovens be preferable depends on the amount of work to be stoved. Ovens of small dimensions may be recommended, as their temperature is more easily kept constant, and one may be filled while the other is engaged in drying. The dipping and oxidising oven process is being replaced by a vacuum process in which the drying of the material and the impregnation are performed in a vacuum plant. The installation comprises: (a) a tank which serves for drying and then for impregnation in the vacuum; (b) another tank in which the product used for impregnation is heated to a temperature which gives it sufficient fluidity; (c) a special surface condenser, which serves to collect the liquid arising from the drying process carried out in the first tank; (d) a vacuum pump for the creation of a vacuum in the first tank and acting as compressor. The windings to be impregnated are dried in the vacuum chamber and the impregnating varnish is introduced by atmospheric pressure on opening the valve in the coupling pipe. By the process of drying and impregnation in the same tank re-absorption of humidity is avoided. In the case of oil varnishes, the drying requires an oxidising treatment, whereas, where the coating is rendered solid by evaporation only, the whole process of drying the material, impregnation and removal of the solvent can be carried out in the same tank. In the case of impregnating com-

pounds, such a form of plant is efficient. It must be pointed out that after impregnation an air pressure of about 50 lb. per sq. inch is applied in the vacuum chamber, so as to force the compound into the windings. The surplus varnish is run off.

For coils and armature windings the addition of a resin or rosin

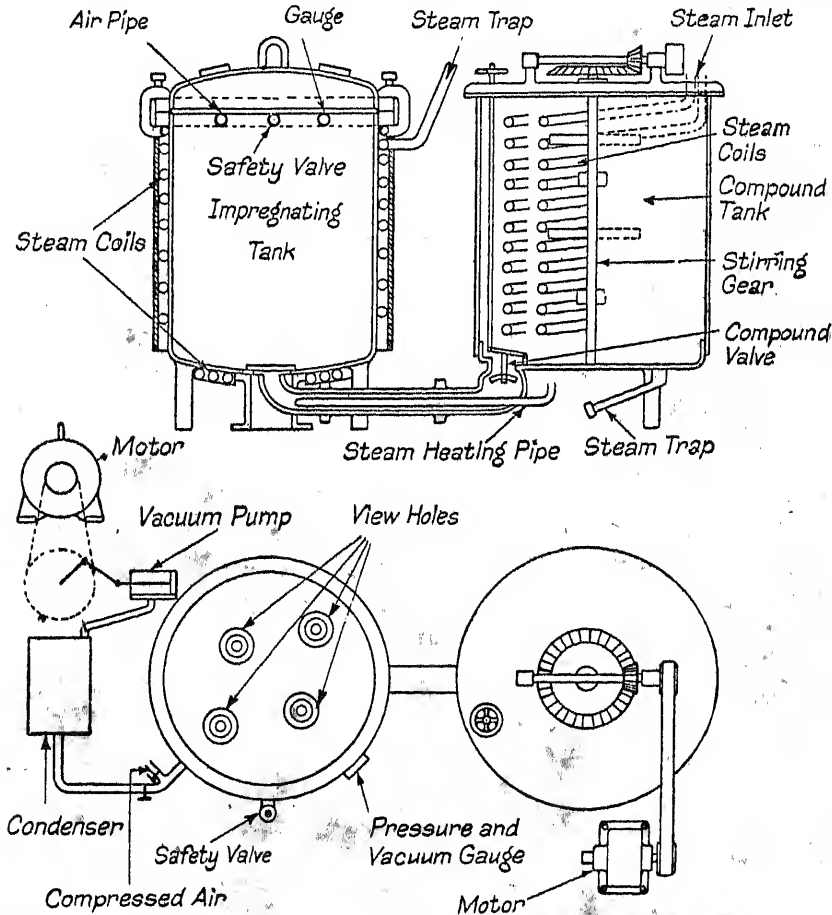


FIG. 21.—Vacuum Impregnation Plant.

(neutralised with lime), forming a gum base with manganese as a drier in the oil, produces an elastic and comparatively hard surface of good dielectric strength and durability. The presence of much resin, although giving greater hardness and resistance to moisture, produces a film which may eventually become brittle. It is advisable by increasing the proportion of oil and controlling the amount of driers to give a material which will retain its flexibility under work-

ing conditions. It is also of value to consider the penetrating power of the insulating coating. If the varnish be too thin, it is apt to give poor dielectric protection, due to lack of body, whereas too thick a varnish also yields poor dielectric strength, due to lack of penetration. It is better to err on the side of good penetration for retaining dielectric strength, because the greatest defect of insulation is due to retained moisture in the cotton covering of the wire, and a varnish which permeates well gives a more completely sealed surface. There is a difference of opinion as to whether it is advisable to coat each strand of the wire completely with a thin, quick-drying oil varnish and then to dip the coils in a more elastic form of oil varnish, contrasted with the method of dipping the coils previously dried in an oil varnish which is forced by pressure into the cotton covering of the wire. In the former process the results are said to show fewer cases of breakdown than in the second, which latter is undoubtedly more easy to carry out.

Where special work is exposed to great changes of temperature and unfavourable hygroscopic conditions, the first method is safer, in spite of the drawback in the time taken in drawing the stoved cotton-covered wire through the thin first-coat sealing varnish. There is no difficulty, under the circumstances, in winding the first-coat treated wire. The only disadvantage is the introduction of another stage in the process of insulation.

For ordinary installations the second or American method is perhaps the most popular (cf. Fleming and Johnson, *loc. cit.*, p. 69). Messrs. Scott, Kingsway, London, describe a vacuum drying and impregnating plant according to their system, which may be consulted to amplify the information given by the line drawing.

The drying oil used is essentially linseed oil, either alone or blended with tung oil. In many cases, the linseed oil employed in varnishes has been thickened previously by heat, but not blown, as it is advisable to keep the acidity of the drying oil as low as possible. The authors have no knowledge of the use of other drying oils in insulating preparations. It is quite likely that oils like soya are used to adulterate the linseed oil without serious detriment to the varnish, provided that they will stove hard in a reasonable time. It is impossible to give in this volume the methods of testing insulating oil varnishes. The reader is referred to the specifications issued by the British Electric and Allied Industries Research Associations, 1924, Techn. Pub., A/S 5 and A/S 9 and Amer. Soc. Testing Materials, D92—21 T, 1922, where full details of the requirements will be found.

(c) THE MANUFACTURE OF PATENT LEATHER

Although patent or enamelled leather can be made in several ways,¹³ the methods to be described are those involving linseed oil. Prior to the enamelling it is most important that the leather should receive a proper preparation. Careful attention is required in the wet work to see that the fibres are not damaged, and it is wise not to carry the swelling too far. After tanning, the leather is fat stuffed with degreas and linseed oil, or degreas and fish oil. Subsequent operations include drying, stretching, etc., and the bellies are damped over with a weak glue solution to give additional strength. When dry the enamelling is proceeded with.

The methods given below have been submitted to Mr. H. G. Crockett for confirmation as a record of published methods. The authors cannot guarantee from their own experience that they are the methods followed in this country, as great secrecy is observed in the treatment of the linseed oil. The French methods mentioned in this section are fuller in detail and are similar to the published English methods, which will be described first.

The prepared leather is first coated with "daub," which is of the nature of a preparing coat for covering the grain surface of the leather with an impermeable finish through which the finishing coats will not penetrate. A special lead-drying oil containing (per gallon of oil) 0.3 lb. of litharge, 0.1 lb. manganese borate, 0.6 oz. burnt umber, and 0.1 lb. Prussian blue is prepared. It is essential that the ingredients should be in as fine a state of subdivision as possible before addition to the oil. The mixture is boiled at 500° F. and kept at that temperature for 6—8 hours until a thin jelly is obtained, allowed to cool, and the temperature raised to 500—550° F. for a further period of 4—6 hours. The film must dry in 24 hours; if it does not, the boiling must be continued for 5—6 hours at 500° F. The temperature is allowed to fall slowly to 100° F., and the jelly is then thinned with petroleum spirit in the proportions of 3 gallons to 10 gallons of oil, so as to produce a thick, viscous mixing. The mixture is applied slightly warm with a wooden sleeker in a japanning stove at 95—100° F. and carefully spread over the grain surface of the leather, the excess being scraped off. After the application of the first coating, the skins are placed in the japanning stove until the coating is quite dry, when they are removed and exposed to sunlight and air for 24 hours. Some manufacturers use a mixture of soluble cotton, dissolved in amyl acetate, for the "daub," instead of the linseed oil coating. The strength of the soluble cotton mixture is about 3 per cent. It must not be

too thin, otherwise it will penetrate into the leather and make it too hard. It is best applied with a varnish brush, the leather being given a good coating and then dried preparatory to applying the black varnish.

The first varnish is made on the lines of the "daub" and may consist of 10 gallons of linseed oil, 5 lb. of Prussian blue, and 3—4 lb. of vegetable black. The oil is boiled for 12 hours at a temperature of 600° F. and the vegetable black must not be added until the completion of the oil-boiling process; moreover, the oil should not be boiled for more than 1 hour after making the addition of the vegetable black. After the application of the "daub," the surface is pumiced and all dust is brushed off. The first coat is applied with a brush. After application of the first coat of varnish, the leather is returned to the japanning stove and dried ready for the finishing coat. For the finishing coat 10 gallons of linseed oil, 2 lb. of Chinese blue, and 2 lb. of manganese borate are boiled at 650—680° F. for 12 hours. The finishing varnish is applied after pumicing the skins in as thin and level a film as possible. After the application of the finishing coat, the leather is returned to the japanning stove, and stoved for at least 24 hours until quite dry. It is advisable to expose the finished leather for at least 2 days to air and sunshine so as to make the enamel more elastic.¹⁴

The principle of the method is to produce a polymerised lead drying oil which is hardened by the iron of the Prussian blue. In the opinion of one of the authors Chinese blue causes less waste and is more easily incorporated.¹⁵

In the French method three coats are used in varnishing leather, the first coat, the second, or blacking coat, and the third, or varnish coat, but all have as a base linseed oil. The oil is carefully selected, and preference is given to Dutch oil which has been tanked for some time and has been refined by a curious process, stated to remove the stearin and palmitin. The treatment consists of the addition of 10 per cent. of its weight of fuming nitric acid, which is added slowly with stirring. After leaving several days, the acid liquor is removed, and after further standing the oil is heated and filtered. In the opinion of one of the authors, this treatment is more of the nature of nitration than for the removal of the saturated glycerides, and may confer on the oil the same advantages as in the case of the nitration of castor oil.

The drying oil is made by addition of litharge and manganese borate. If these substances be heated for too long a time with the oil, there is a possibility of a darkening in colour taking place, and

it is advisable therefore not to add them until after the cooking. Cooking is done over an open fire in a pan or copper, a lid being suspended over the latter, so that it can be shut down to prevent ignition of the contents. A jacketed pan connected with superheated steam may also be used, and the oil is first heated up to 150°, at which point it is held until frothing ceases. The temperature is then taken up to 250°, when it will change to a bluish-green colour. Any albuminoid material will also coagulate at this temperature, and can be removed later. The pot is now covered and allowed to cool slowly. While still hot, the oil is transferred to iron tanks, where it is stored and clarified by sedimentation.

This oil is used for the preparation of the first coat. It is heated quickly in a copper vessel, one-third full, to a high temperature with the necessary materials. For 20 kilos. of heated linseed oil there will be required 50 gms. of litharge, 1400 gms. of Prussian blue, 400 gms. of lead acetate, 300 gms. of bichromate of potash. The whole is heated at 200° until the proper consistency has been obtained. The consistency can be determined by the following signs: the colour of the froth turns a dark brown, and if a drop of the oil be placed upon a piece of glass it can be drawn out into a long thread. At this point the varnish is put into a closed vessel, taking care to leave any deposit in the pan. Before using, the varnish is thinned with its own weight of turpentine, so that it will flow easily, and the mixture filtered through fine gauze.

• *Application to the Leather.*—The leather is first degreased with turpentine and dried. In order to get the necessary suppleness it is grained and put into frames. The coating of varnish is then evenly applied and the leather again put into frames and exposed to the sun to dry. When dry the varnished surface is worked over with an artificial pumice stone, No. 2, free from dust, while still in the frame. The leather is now ready to receive the second or black coat.

The black varnish for the second coat is made with 20 kilos. of boiled linseed oil and 40 gms. of litharge, heated together for 3 hours at 200°. Directly afterwards 6 kilos. of ivory black, 600 gms. of lead acetate, 200 gms. of manganese borate and 200 gms. of Prussian blue are added and the boiling is continued for 20 hours. This process is complete when the mass has the consistency of tar, and when a drop placed on glass can be drawn into a thread 5 cm. long. Before using, 1½ kilos. of the oil will require 2½ kilos. of turpentine and ¾ litre of light petroleum for thinning. Three hundred gms. of Prussian blue and 300 gms. of lampblack are

ground to a fine powder with 200 gms. of turpentine and then added to the oil. The varnish is now applied to the leather, and the work then put into frames in a stove at 50—55°, where it is left for 8—10 hours. It is then exposed to the sun until the surface is no longer tacky. Each hide or skin is now placed upon a table covered with felt and pumiced. After re-framing, the varnished surface is washed with water and allowed to dry before proceeding to the application of the third coat.

The varnish for the third coat consists of linseed oil (50 kilos.) heated for an hour at 240°, and after removing any scum the following substances are added: Prussian blue, 2 kilos.; lead acetate, 750 gms.; zinc sulphate, 750 gms.; manganese acetate, 300 gms.; lampblack, 500 gms., and litharge, 850 gms. The oil is heated in the usual way, until the desired thickening has taken place. The varnish is allowed to cool and turpentine is added. It might be mentioned that all three varnishes used should be warmed to 50—60° before being applied. A soft brush is used for the application and the operator works from head to tail in a regular manner. The leather is put into frames and stoved at 55° for 15 hours, and finally exposed to the sun or put in a dry place, until the surface has set and is free from tackiness. The varnished surface is lightly cleaned with a chamois leather, measured and sorted, etc.¹⁶

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CHAPTER VIII

THE PROPERTIES OF DRYING OILS FROM A COLLOIDAL STANDPOINT

ALTHOUGH linseed and other drying oils may be considered as solutions of mixed glycerides of unsaturated fatty acids, properties are manifested by them which are difficult to explain from the standpoint of solutions. In their oxidation, with the formation of a linoxyn, the relationship of the product is not strictly that of a new substance in solution in the original oil. In the thickening of drying oils by heat, the changes which occur are not such as can be fully accounted for from a chemical standpoint by the polymerisation of one or more of the compounds. On the other hand, changes of aggregation of suspensoid material in a disperse medium are also insufficient to account for the properties exhibited. J. W. McBain¹ has commented on the excess of speculation from which the subject of colloids has suffered in the absence of precise and definite experimental evidence, and in his opinion the more carefully a colloid is studied the less colloidal it is found to be. Characteristics of the so-called "emulsoid" class of colloids are shown in the behaviour of drying oils under certain conditions. It must be confessed that little systematic investigation has been carried out, and there is a tendency to explain phenomena by comparison with the behaviour of other systems. It is presumed that the reader has some acquaintance with the properties of colloids as well as of suspensoids in a water medium. In the "emulsoid" class the disperse system for drying oils must be considered in some cases as containing components in common with the disperse medium. Nevertheless, under certain conditions, the drying oils are components of ordinary water emulsions where the presence of a membrane, produced by a third substance (emulsifier) around the globules of one of the components, renders the dispersion of one of the two fluids stable, and prevents separation into two liquid phases. This form may be illustrated in water paints, containing drying oil, where the drops of oil are coated with a film of soap and thus kept apart and suspended in water. The theory of emulsions and emulsification is fully discussed by W. Clayton in "The Theory of Emulsions and Emulsification" (1923). Two types of emulsions are met with in systems containing drying oils. The first, or oil-in-water type, is shown in water paints; the second, water-in-oil, type is shown in the milkiness of drying oil films immersed in water. According to the present accepted theory of emulsions, an adsorbed film or membrane surrounds the dispersed globules of either oil or

water. The emulsifier for water paints is a partially water-soluble colloidal substance. The colloidal emulsifying agent is absorbed at the dineric or boundary surface and forms a film. In the case of water emulsions, the reversion of the emulsion by electrolytes will depend on the nature of the adsorption of ions. An excess of adsorbed positive ions on this film leads to water-in-oil emulsions, an excess of negative ions produces the opposite type.

Bhatnagar² generalises as follows: all emulsifying agents which are wetted by water and which have an excess of adsorbed negative ions will yield oil-in-water emulsion, while those wetted by oil and having an excess of adsorbed positive ions give water-in-oil emulsions. It is evident that a trace of an alkaline soap (potash soaps are better emulsifiers than soda soaps) will favour an oil-in-water emulsion, whilst a lead soap would favour a water-in-oil emulsion, especially as it is wetted by oil. The life of the water-in-oil emulsion depends also on the metal, *e.g.*, a calcium soap, 1 hour, magnesium soap, 2 days, zinc soap, 24 days, silver soap, 1 day, iron soap, 10 days, aluminic soap, 7 days.³

It is advisable to make reference here to the wetting of surfaces. When a liquid impinges on a solid there is a definite angle of contact, constant for a given solid and a given liquid, this being the angle between the surface of the liquid at the point of contact and the solid liquid interface.

When a liquid wets a solid the contact angle is zero.

In other words, the difference between the surface tension* of the solid and interfacial tension at the solid liquid boundary must be equal to or greater than the surface tension of the liquid; thus if a powder be shaken with two liquids *A* and *B*

$T_{BS} > T_{AB} + T_{AS}$ (solid remains in *A*).

$T_{AS} > T_{AB} + T_{BS}$ (solid remains in *B*).

$T_{AB} > T_{BS} + T_{AS}$ (solid goes to the interface, tending to separate the two liquids).

(T_{BS} = interfacial tension between liquid *B* and the solid.

T_{AS} = interfacial tension between liquid *A* and the solid.

T_{AB} = interfacial tension between the two liquids.)

When none of the three tensions exceeds the sum of the other two the powder goes to the interface and the three phases meet at a certain contact angle. All finely-divided solids which act as emulsifiers appear in the interface between two emulsion liquids, and their distribution is determined as follows: Consider a solid sphere *S* at the interface between liquids *A* and *B*,⁴

Equilibrium attains when $T_{AB} = T_{BS} + T_{AB} \cos \alpha$, where α is the angle of contact. If $T_{AS} > T_{BS}$, then $\cos \alpha$ is positive and $\alpha < 90^\circ$, the greater portion of the solid being in the liquid *B*. If $T_{AS} < T_{BS}$, then $\cos \alpha$ is negative and $\alpha > 90^\circ$, more of the particle is immersed in the liquid *A*.

The superficial arrangement of the molecules in the liquid must be considered; for example, in the case of oleic acid, one molecule in thickness, on the surface of water, the COOH group is in contact with the water.⁵ The emulsifier is adsorbed at the interface and acts as a bridge between two dissimilar liquids. The tension is diminished at the interface, whereby increased subdivision of one liquid in another is permitted. The orientation is such as to reduce the free energy to a minimum, and on the packing and molecular orientation of the emulsifier at the dineric surface depends the type of emulsion promoted.⁵

There are no published investigations on the behaviour of pigments in drying oils and water-forming water-paint systems, but the investigations by Bhatnagar, on lead oxide in mineral oil and water, are of interest as illustrating reversion of the emulsoid type.

He found that emulsions, containing 15 c.c. each of the oil and aqueous phase, were stable and of the water-in-oil type in the presence of various amounts of KCl, K_2SO_4 and $Al_2(SO_4)_3$, except when the concentration of KCl reached 0.005 gm.-mol. per cent., where the stability was poor. With K_3PO_4 and KOH inversion occurred.

Type of emul- sion.		Type of emul- sion.	
K_3PO_4	{ 0.0021 gm.-mol. % Win O (stable) 0.008 " " O in W "	KOH	{ 0.002 gm.-mol. % Win O 0.004 " " O in W

The connection between water absorption of drying-oil films and their permeability has been investigated by one of the authors. A copal linseed oil varnish film containing lead and manganese was compared with a rosin ester tung-oil varnish, containing not lead but manganese as drier. The permeability of the two films by water vapour was compared, and it was found that they were equally permeable, but were impermeable to salts in water solution, thereby showing the semi-permeable character of the membranes. Films of the two varnishes were found to have very different water absorptions. The copal linseed-oil film became cloudy owing to emulsification, whereas the wood-oil film remained clear. The accompanying graph shows the comparison. It must be noticed that the permeability is steady. The emulsification forces act

strongly to hold the absorbed water and the film appears to act as a sponge. The practical effect is a weakening of the adhesion of the linseed oil surface, with a loss of lustre due to distension of the surface layer. The phenomenon is essentially internal and appears

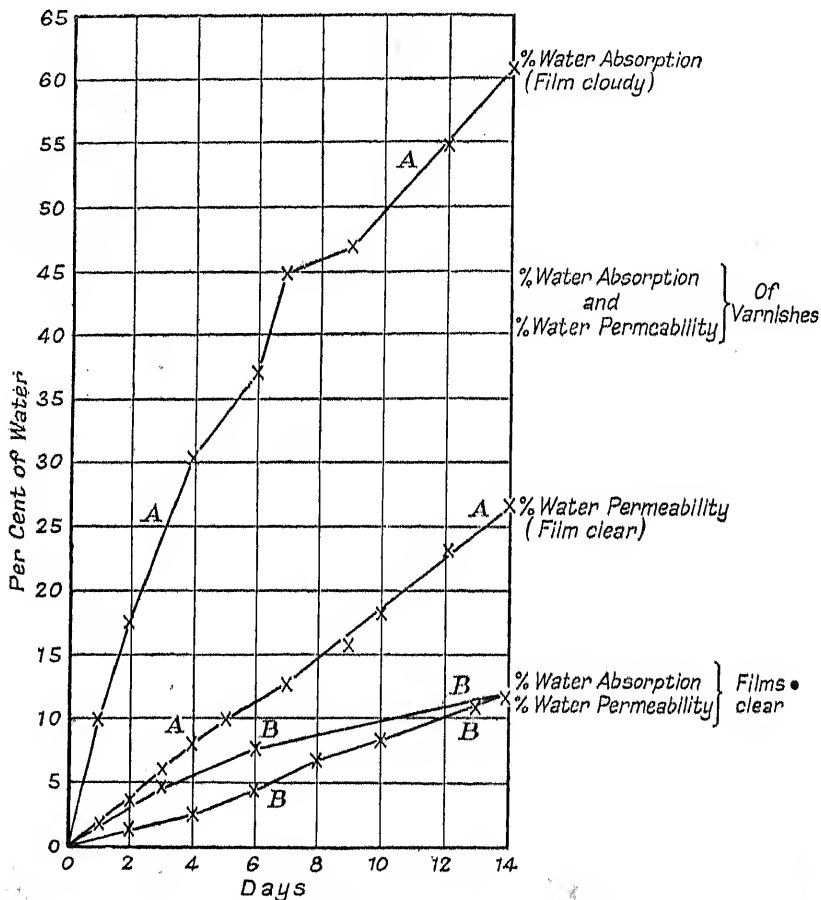


FIG. 22.—Comparison of Rates of Water Absorption and Water Permeability of Varnishes.

A. Elastic Copal Varnish.

B. Spar Varnish.

to be independent of the polarity of the surface. Such polarity is absent in the case of the linseed-oil film, whereas that of wood oil is strongly polar. There is a preference for wood-oil films, although the protective character of the linseed-oil film is not much inferior to that of wood oil.

The application of the principles of colloids to the polymerisation of drying oils, has been referred to in the previous chapter,

and it may be advisable to consider the colloid aspect somewhat further by a comparison with the properties of gelatin and water and tung oil. The viscosity changes in the two systems are shown in the accompanying graphs (Figs. 23 and 24). The thickening of tung oil on heating involves an apparent reduction in the bromine value, with an increase in viscosity, but at the transition point of the oil to a gel the increase in viscosity is very great, whereas there is hardly any change in the bromine value. It is inadvisable to neglect the special chemical characteristics of drying oils in connection with their behaviour when heated. Although poppy-seed oil and tung oil contain glycerides of linolic and elæostearic acids respectively, differing only in the arrangement of the ethenoid linkages, never-

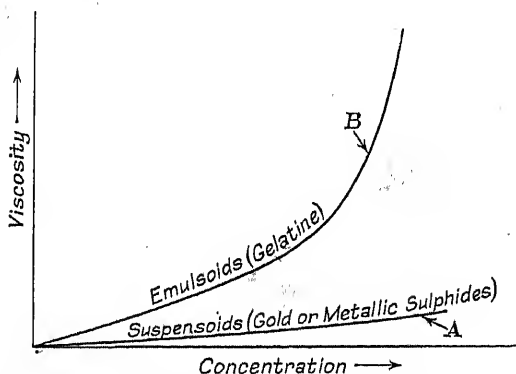


Fig. 23.—Diagram illustrating the Relation between Viscosity and Concentration in Different Types of Colloids.

theless the difference in their behaviour towards heat is very marked. The thickening of linseed oil is dependent on the chemical composition and is connected with the presence of three ethenoid linkages as well as the glyceryl radicle. The thickening of the oil, however, cannot be satisfactorily explained on any form of intra-molecular polymerisation. There is an extra-molecular aspect to be considered. The variable iodine values of the thickened oil, the production of less polymerisable acids and methyl esters, require some special explanation. Nevertheless in the case of linseed oil there is evidence of shifting of the ethenoid linkages during the long period of heating necessary, with the result that the properties of the ordinary components of linseed oil cannot be identified, even after the disappearance of the viscous state. In the case of tung oil, where the heating is for a shorter period, the products separated are easily transformed into derivatives of the original elæostearic

acid. Comparison with a gelatin jelly containing drops of water may be of interest, as showing the extent of the analogy between the two systems. W. D. Bancroft⁶ has summarised the recent knowledge on the properties of jelly. He states that a concentrated gelatin jelly, with drops of water suspended in a gelatin rich phase, should not be considered to have a honeycomb structure in the same sense as that of an emulsion. With an emulsion there is a film of a third substance around the dispersed drops, and there would still be an emulsion if the outer phase could suddenly be

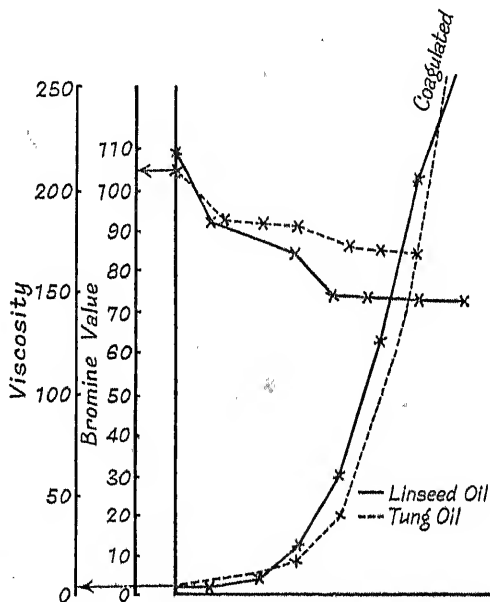


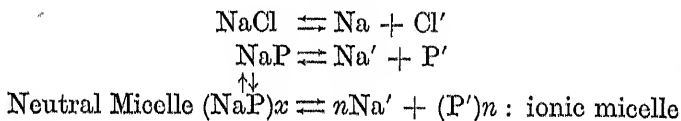
FIG. 24.—Viscosity and Bromine Value Changes of Linseed Oil and Tung Oil (H. Wolff, *Z. angew. Chemie*, 1921, **37**, 730).

made fluid. Under similar conditions the drops of water in the gelatin jelly would undoubtedly run together. A gelatin jelly of the type under consideration is merely a viscous medium in which water is dispersed. In the case of emulsions the type depends on the nature of a third substance and not on the relative masses of the two liquids. If a gelatin-water mixture were of a water-in-oil type at any concentration it would be a water-in-oil type at all concentrations. Much stress has been laid at times on the alleged fact that ultra-microscopic examination has shown that jellies have a sponge structure, and not a honeycomb structure, but it is now admitted that these two structures are indistinguishable by the ultra-microscope.⁷ It has been stated that with gelatinous pre-

precipitates, as with jellies, there is a binary system in which each constituent peptises the other. A jelly is a completely transparent elastic mass, "gels" being flocculent and gelatinous precipitates. Jellies may be obtained without marked interference with the equilibria in the solution; gels cannot. Soap solutions or jellies are not emulsoids.⁸ The gelatin-rich phase will always contain peptised water and the water-rich phases will always contain peptised gelatin. This point must not be overlooked in any consideration of the polymerisation of oils. A dilute colloid solution of gelatin in water will consist essentially of turbid drops of a gelatin-rich phase dispersed in water. With increasing concentration of gelatin there will be a tendency for the separate drops to coalesce into larger drops. If they are too viscous to do this, they may coalesce partially, forming threads, or to a still lesser extent forming a chain of beads. In this latter case it is not necessary that the drops themselves should be in actual contact. In the preliminary stages it may only be the adsorbed films of water which are in contact, just as happens with a plastic mass of sand and water. With increasing concentration of gelatin, loose chains may be formed which will then pass into a net or sponge structure of which a granular jelly is an extreme form. In jellies of this type, both phases are continuous and form an interlacing system. With still further increase in the gelatin content, the water may be dispersed as definite drops in the gelatin-rich phase. While this might be called a honeycomb structure, it is probably better to reserve "honeycomb" for structures in which the cell-walls are thin relatively to the diameter of the cells, and it may be desirable to restrict it to cases like that of an emulsion with a distinct film round the drops. Owing to the comparative ignorance in regard to jellies, it is not known to what extent increase in the concentration of gelatin, for instance, causes the mass to fill up with chains or filaments of the same diameter, or to what extent each filament increases in cross sections.

In a discourse before the Royal Institution¹ on March 20, 1925, on "Soaps and the Theory of Colloids," J. W. McBain discussed the micellar theory, which was deduced from a study of colloidal solutions. Selmi and Nägeli concluded that, if colloidal matter were to be explained, it must not be assumed that the chemical molecule is the unit, but that there must be a larger unit, which Nägeli called the "micelle." These colloidal units were the bricks, out of which larger structures than colloids could be made. He considered that a typical colloid, like the starch grain, was composed

of a large number of these small crystalline particles. McBain prefers the conception, without inferring any crystalline structure, that the micelles can be put together to build up larger structures. The work on soaps has led to the consideration of two kinds of micelles, one highly charged, like an ion, called the ionic micelle, and the other nearly neutral; these latter are the bricks from which larger structures are built up. Modern ideas of polarity explain the formation and stability of these micelles. For example, in sodium palmitate the palmitate ions polymerise to large hydrated units (micelles), the colloidal palmitic acid adsorbing hydroxyl ions, like silicic acid does, and being peptised by them.⁶



In considering the thickening of oils the conception of nearly neutral micelle seems to be especially applicable.

The neutral micelles (sodium palmitate) may be visualised by considering each particle as a pair of military hair-brushes, in which the bristles represent the hydrocarbon chains of the molecules arranged parallel to each other in sheets, two such layers being put together hydrocarbon to hydrocarbon. The two backs of the brushes on the outside represent the hydrate layer and the un-ionised electric double layer. In a thickened oil the unsaturated linkages may cause attraction of the visualised hydrocarbon chain bristles, but the presence of ionic micelles is out of the question.

When the hydrosols of gelatin, soaps, etc., are employed for the study of the reversible change sol-gel, the interpretation of results tends to be unduly complicated by the disturbing influence of hydrolytic reactions. Simpler relations are to be expected in non-aqueous media.

E. W. J. Mardles,⁹ using cellulose acetate in benzyl alcohol, recognises three stages in the process of gelation: (1) coalescence of fine to large particles, (2) aggregation of these large particles into clusters, (3) the linking of the clusters to form a rigid jelly structure. The dependence of the time factor, associated with these several changes, on the concentration and temperature of the organosol has been elucidated by measurements of the light-scattering power (Tyndall number), viscosity, density and rigidity. It may be presumed that, in the gelation of oils, the process proceeds similarly to the above. It has been pointed out that the drying oil gels often contain free oil. How this oil is enclosed is not definitely known.

Zsigmondy¹⁰ considers that water in soap curd or gel is present neither in solution nor as water of crystallisation, but is enclosed in capillaries formed by a framework of fine needle-like crystals of the soap, ultra-microscopic in two dimensions.

Another phenomenon in the behaviour of colloid systems containing water is shown in dialysis, where the liquid in the dialyser is apt to set to a jelly just before the colloid is entirely pure; in other words, just as the peptising agent is brought slowly below a critical value.¹¹

In a recent report on the chemistry of hide and gelatin¹² the influence of the chemical composition of gelatin on its swelling and coagulation properties is shown. The work of Proctor, Wilson and Loeb has demonstrated that swelling of proteins in acid and alkaline solutions is due to the formation of ionisable compounds. The properties of gelatin jellies outlined above may be compared with those of drying oils, water being replaced by the oil, minus some of its unsaturated components and non-ionisable, and gelatin by a component which is highly unsaturated and capable of union with, or attraction for, molecules or aggregates of the same chemical composition. The resulting system will therefore contain this highly unsaturated part associated with the unchanged oil in a medium of changed oil.

Many of the phenomena which occur when China wood oil is thickened and coagulated by heat are comparable with the behaviour of a gelatin-water system. In tung oil the equilibrium of the thickened fluid would seem to be at 50 per cent. of associated components, and any increase in the amount of these causes the system to set to a jelly. The gelation can be prevented by the presence of small quantities of apparently inert substances, of which rosin is most generally used. In other words, the rosin acts as peptising agent. The addition of substances like glycerol or sulphur has a marked effect in preventing coagulation. One per cent. sulphur or 5 per cent. glycerin is stated to prevent solidification of tung oil even at 280°. It is quite possible, by a suitable treatment with rosin, to produce wood oil in large quantities which will refuse to coagulate at temperatures of about 300°. Such changed wood oil is unlike the original in properties, and there is indication of shifting of the ethenoid group at that temperature to produce an isomer of wood oil which resembles in its properties an oil of the cotton-seed nature. It has been shown that in coagulated wood-oil jelly, which is formed, like all jellies, with an evolution of heat, the spongy mass contains unchanged tung oil and the jelly is either a sponge or a

honeycomb containing unchanged oil, and investigations on the gelatinised wood oil, which is saponifiable by alkalis, have shown elæostearic acid to be present. Further investigation of the products of gelation of this oil are very desirable. It has been pointed out that the thickening of the oils is connected with the presence of ethenoid linkages in special positions in the long carbon chain. Such unsaturated components have the power of forming aggregates, adsorbing the oil which is the dispersion medium, and remaining in a fluid condition depending on the temperature and the presence of small quantities of peptising agents. It has been claimed that in thickened linseed oil there is evidence of a colloidal and emulsoidal condition involving adsorption, especially of the acid components, which interferes with the satisfactory determination of the acidity unless a liquid is added which will destroy the adsorbing effect. The use of benzene in the estimation of the acidity of linseed oil is advocated on the ground that it will prevent this absorption of the oil acids by the colloidal components as shown in the following table:—

Acidity of linseed oil in the presence of ethyl alcohol	0.92—1.01
" " (thickened at 260°) in the presence of ethyl alcohol	8.8 —11.8
" " in the presence of benzene and ethyl alcohol (1:1)	0.99—1.05
" " (thickened at 260°) in the presence of benzene and ethyl alcohol (1:1)	14.36—14.38

According to H. Vollmann¹³ the colloidal character is shown by its stabilising action on suspensions of finely divided pigments, but which constituents of the oil form the disperse phase is unknown.

There are a number of instances which may be quoted as showing the close similarity of the properties of drying oils and water gels—properties which are influenced by small quantities of apparently inactive substances, or by changes in the acidity of the system. An instance may be given of the behaviour of certain linoleates, dissolved in mineral spirits containing aromatic hydrocarbons. The linoleates in solution will often set to a gel form, but by the addition of a trace of rosin will resume the liquid condition. Again a mixture of a resin with a drying oil and a petroleum thinner may be stable with certain proportions of the petroleum spirit, but an increase of that component, beyond a certain amount, will cause complete separation of resin and oil. The separation of the gel may be prevented by the addition of traces of an acid, *e.g.*, salicylic acid, which increases the dispersion of the jellying component of the system and prevents coagulation. Another interesting case is the

behaviour of petroleum and Prussian blue with and without linseed oil. In the former case the blue solution can be filtered apparently unchanged, whereas, in the absence of the oil, the blue colouring matter remains on the filter. Linseed oil acts as a protective colloid, linking up the petroleum with the pigment.

The comparison may be carried further in the consideration of the properties of oxidised oil films (linoxyn). Linoxyn shows, like gelatin, swelling with liquids such as light petroleum, benzene and tetralin, the last having the greatest action. It is due to the swelling phenomenon that the action of benzol and alcohol is made use of in paint removers. In the oxidation of drying oils there is a similar want of connection between the concentration of the oxidised oil and the viscosity. The great variation of viscosity with slight variation in composition has been noticed in connection with the thickening of drying oils. W. Schlick ¹⁴ has put forward a number of such cases in connection with the properties of thickened drying oil, oxidised oil films and the properties of metallic resins in non-aqueous media. Such comparisons are of great importance, if not carried so far as to neglect the chemical properties of drying oils. Of special value is the reference to syneresis, which is easy to explain if linoxyn is considered as a lattice-work system, in which a semi-solid film encloses a liquid phase containing unoxidised oil. The behaviour of linoxyn from a colloid aspect has already been discussed on p. 105. There are several other facts which may be considered: (1) the influence of light on linseed oil, whereby its viscosity is increased and likewise its power to absorb oxygen. This power disappears when the oil is kept in the dark, and although the explanation is given by Schlick on colloidal grounds (*viz.*, light produces a reduction in the dispersion of the whole system, and an increase in the oxygen absorption indicates a case of sorption catalysis), it may have another explanation in the disappearance of the autocatalyst, peroxide, in the dark, which substance is considered by some to act as a stimulus in the drying of the linseed-oil film; (2) in the case of raw perilla oil compared with the heated oil (p. 57) the difference is stated to be due to surface tension effects; (3) the ageing of varnishes is accompanied by changes in viscosity and in the dispersion of the gum-oil-thinner aggregates. The problems of oil absorption of pigments and the behaviour of resins in drying oils will be dealt with in other volumes of the series.

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CHAPTER IX

THE ANALYSIS OF DRYING OILS

THE vehicle of the liquid portion of a paint or enamel may contain a drying oil, turpentine, mineral oil distillates and resin varnishes. On the other hand, varnishes contain resins, drying oils and thinners, turpentine or turpentine substitutes. The separation of the vehicle of a paint from the pigment will be described in the volume on the Analysis of Paints by Dr. J. J. Fox and T. H. Bowles.

The separation of a drying oil from resin, turpentine or turpentine substitutes has been described under the analysis of oil varnishes.¹ The most important drying oils met with in paints and varnishes are linseed and China wood oil. Other drying oils, such as walnut, poppy, hemp, niger, soya bean and menhaden, are used only for special purposes, the two first being components of artists' colours, and not of commercial paints and varnishes.

The Examination of Drying Oils.—In a complete examination of a drying oil it is advisable to determine: (1) specific gravity, (2) iodine value, (3) acid value, (4) saponification value, (5) unsaponifiable matter, (6) moisture, (7) the percentage of oxidised acids, (8) the refractive index, (9) the ether-insoluble bromide value of the oil or of its component acids, (10) the drying time of the oil against a standard linseed oil, (11) mucilage, (12) colour and (13) the viscosity.

Nos. 1, 2, 3, 4, 5, 8, 10, 11 and 12 are generally essential. The determination of the refractive index [1.5180 (20°)] is of importance for China wood oil.

Specific Gravity.—Either a specific gravity bottle or a Sprengel tube may be used, but generally the Westphal balance is preferred, especially when considerable quantities of the oil under examination are available and it is not too viscous. With the exception of China wood oil (s. g. 0.940 at 15.5°) all the drying oils have specific gravities lying between 0.925 and 0.933 . Bodied oils which have been produced by the action of heat have specific gravities increasing with viscosity up to 0.9912 (15.5°) and 1.000 .

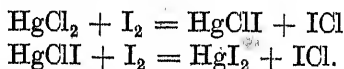
Iodine Value.—The most important methods for the determination of this value is:—(1) the Hübl method with a modification proposed by Waller and (2) the Wijs and Hanus methods.

The Hübl method requires the following solutions: (a) an iodine solution, which is prepared by dissolving 25 gms. of iodine in 500 c.c. of 95 per cent. alcohol, is mixed with 30 gms. of mercuric chloride dissolved in 500 c.c. of 95 per cent. alcohol. These solutions should be mixed as required and the mixture be allowed to stand 24 hours before use; (b) a standard solution of sodium thiosulphate and a

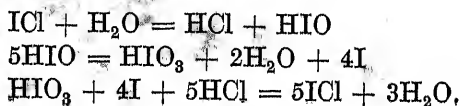
solution of potassium iodide free from iodate. The solvent for the oil is generally chloroform or carbon tetrachloride, which should be pure. Ether may not be used, but benzene (free from thiophen) or glacial acetic acid may be employed.³

The determination of the iodine value is carried out as follows : from 0.15 to 0.18 gm. of drying oil (0.2—0.3 gm. of semi-drying oil) is weighed off accurately into a bottle of 500—600 c.c. capacity, provided with a well-ground stopper. The oil is dissolved in 10 c.c. of chloroform or carbon tetrachloride, and 25 c.c. of iodine solution are run in from a pipette. In order to prevent loss of iodine by volatilisation, it is advisable to moisten the stopper with potassium iodide solution. The oil in the solvent and the iodine solution must give a clear mixture, otherwise more solvent must be added. The mixture must exhibit a dark brown colour after 12—18 hours in the case of drying oils, otherwise 25 c.c. more of the iodine solution must be added to maintain excess of iodine; 15—20 c.c. of potassium iodide are added and the mixture is well shaken and diluted with 400 c.c. water. If a red precipitate of mercuric iodide appears, more potassium iodide must be added. Standard thiosulphate solution is run in until both water and solvent layers are only slightly coloured, starch solution is added, and the titration finished in the usual manner. Immediately before or after the titration with thio-sulphate, 25 c.c. of the original iodine mercuric chloride solution are treated in the same manner so as to form a blank experiment. The difference between the amounts of iodine found, calculated in terms of iodine to units per cent. of the sample, will give the iodine value. It is necessary that 2 gram-atoms of iodine for 1 gram-molecule of mercuric chloride be present. The values obtained by Hübl's method are quite concordant, provided an excess of iodine not less than the amount actually absorbed has been employed, and the operations are performed under identical conditions.

The scheme of the Hübl reaction may be expressed as follows :—

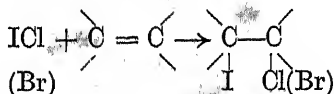


The reaction, which is incomplete and reversible, is best represented by the equations given above. In the presence of water the following reactions may occur simultaneously :—



Of the reaction products, HIO and HIO_3 will react in the presence of hydrochloric acid to give iodine.

In Waller's modification, the hydrochloric acid used inhibits the reaction represented by the first of the second series of equations and prevents the formation of hypiodous acid, which would oxidise the alcohol and so disturb the equilibrium. In Wijs' modification,⁵ the iodine solution consists of iodine trichloride and iodine in the proportions to give iodine monochloride which are dissolved separately in glacial acetic acid or the iodine monochloride is prepared by passing dry chlorine into iodine dissolved in good glacial acetic acid. The Wijs solution is allowed to react with the drying oil in the same manner as the Hübl, but for a much shorter time; half an hour to six hours may be required according to the unsaturation of the glyceride. If acetic acid reacts with the oil under examination, the Hübl solution must be used. The Hanus modification contains iodine bromide and is considered by American chemists to be superior to the Wijs solution, and its use is recommended in American standard specifications of linseed oil. The principle of the Wijs or Hanus method is simple :—



Wijs' Modification of the Hübl Process.—Wijs' iodine solution⁵ may be prepared in two ways :—

(a) 7.5 Gms. of iodine trichloride and 8.2 gms. of resublimed iodine are dissolved separately in recrystallised glacial acetic acid on the water-bath, taking care that the solution does not absorb moisture. The two solutions are poured into a litre flask which is then filled up to the mark with glacial acetic acid. A more convenient way is to dissolve the contents of a 10 gm. tube of iodine trichloride in 300 c.c. of glacial acetic acid, and add a 2½ per cent. solution of iodine in the same solvent until the iodine is slightly in excess. The mixture is then made up to 1 litre with freshly-recrystallised glacial acetic acid. *The mixture is stabilised by heating to 100° for 20 minutes.*

(b) Dissolve 13 gms. of iodine in a litre of good glacial acetic acid, withdrawing 100 c.c. for later use, and pass dry chlorine into the iodine solution until the brown colour changes to a clear orange tint. The iodine solution held in reserve is now added until the colour of the solution becomes faintly brown. The slight excess of iodine prevents the formation of iodine trichloride. *The solution is*

stabilised by heating on a water-bath or on an electric heater to 100° for about 20 minutes, and is kept in the dark in a well-stoppered bottle. The solution maintains its strength for several months if pure materials have been employed. The glacial acetic acid used must be freshly frozen out, and should give no green tinge on heating with potassium bichromate and concentrated sulphuric acid, showing freedom from formic acid.

The Wijs' solution is allowed to react with a drying oil in the same manner as the Hübl, but for a much shorter time; half an hour to six hours may be required according to the degree of unsaturation of the glyceride. If acetic acid reacts with the drying oil the Hübl solution must be used.

Details of the Method.—0.5 Gm. of a drying oil is dissolved in 10 c.c. of purified chloroform or carbon tetrachloride and 25 c.c. of the Wijs solution are added, taking care to moisten the stopper of the bottle containing the mixture with potassium iodide solution, and allow to stand for 1 hour. In the case of oils having a high iodine value, like linseed, it is advisable to allow the mixture to stand for 2—3 hours. The stopper and neck of the bottle are washed down with 15 c.c. of a 10 per cent. potassium iodide solution and 100 c.c. of distilled water added, and the excess of iodine titrated with standard sodium thiosulphate solution. Towards the end of the titration about 2 c.c. of the starch solution are added and the contents of the bottle are shaken vigorously after each addition of the thiosulphate solution until the contents of the bottle are colourless.

A blank test, using 10 c.c. of the oil solvent and 25 c.c. of the iodine solution, must be done with each set of estimations. The result is expressed as the percentage of iodine combining with the oil.

Sundberg and Lundborg state that the Hanus method gives results with fats which agree closely with those found by the Hübl method; ⁶ Wijs' method gives higher results. In the case of linoleic acid * the Hübl value lies nearer to the theoretical than does the Wijs value. ⁷ Marshall proposes the use of carbon tetrachloride, and Aschmann prepares a solution of iodine trichloride in water by passing chlorine into potassium iodide solution until the iodine liberated is dissolved, and after filtering from potassium iodate the solution is allowed to react with a chloroform solution of the oil or fat for 24 hours. The values obtained lie between those obtained with the Wijs and Hübl solution. Kolber and Rheinheimer prefer

* Linoleic acid is the name given to a mixture of oleic, linolic and linolenic acids obtained from linseed oil.

Wijs' method because of the greater stability of the solution and the rapidity of the process.⁸ MacLean and Thomas⁹ have investigated the behaviour of sterols (cf. cholesterol) with the Hübl and Wijs reagents; with sterols, the Hübl solution gave values approximating to those required by the number of double bonds believed to exist in the sterol molecule. With the Wijs reagent the results may be twice as high as those obtained with the Hübl solution, and vary greatly with the temperature, time of contact, and proportion of the reacting substances. The difference in behaviour of the two reagents appears when they react with the sterols (not with reduced sterols) and with the resinic acids, possibly also with the naphthenic acids, though in the latter case definite substances of known constitution have not been investigated. The effect appears to be due to the influence of the glacial acetic acid used in the solution as solvent for the iodine trichloride, and affords evidence that a considerable amount of substitution takes place. The substitution effect is particularly noticeable when a condensed ring-nucleus containing one double bond reacts with Wijs' solution; thus abietic acid containing two double bonds and dihydroabietic acid, containing one double bond, give identical values with the Wijs solution, so that substitution must be much greater in the reduced derivative. Anthracene reacts similarly with Hübl's and Wijs' solutions, giving high iodine values in both cases, but phenanthrene and retene (isopropyl-dimethylphenanthrene) are hardly affected by Hübl's solution, but absorb considerable amounts of iodine from Wijs' reagent. For drying oils Wijs' method may be recommended as most convenient, but in dealing with ring compounds the Hübl method is perhaps safer. Wijs' method gives accurate results with tung oil, but 2 units lower than with the Hübl method.¹⁰

Acid Value.—The acid value may be expressed as the number of milligrams of potassium hydroxide required to neutralise 1 gm. of oil. It is also stated as a percentage of free oleic acid in the oil, this acid being selected as a typical fatty acid occurring in vegetable oils. The acid value of a drying oil is a variable, depending on the quality of the sample and on the mode of extraction of the oil from the seed. Rancidity and oxidation both increase the acid value. For the determination of the acid value a mixture of 50 per cent. of alcohol and benzene is used as the medium for the oil. It has been found that such a mixture gives a more reliable result than when alcohol alone is used.¹¹ Acid value of linseed oil, 1.3; soya oil, 0.8—3.0; perilla oil, 6.7; China wood oil, 2—3; menhaden oil, 5—8; Para rubber-seed oil, 0.6—5.

Saponification Value.—The saponification or Köttstorfer value represents the amount of potassium hydroxide required to neutralise the free and combined acid constituents of a fat or oil, and is expressed in terms of parts of potassium hydroxide per 1000 parts of the fat or oil. The saponification value as determined by the usual method includes the alkali required for the neutralisation of any free acid in the oil, and the acidity must be subtracted from the Köttstorfer value to give the true saponification value.

The values for a few principal drying oils are as follows: linseed oil, 192.5; China wood oil, 193; perilla oil, 189.6; soya oil, 193; Para rubber-seed oil, 206; poppy-seed oil, 195.

Unsaponifiable Matter.—The unsaponifiable matter in fats and oils includes all substances which are insoluble in water, but soluble in the fat solvents specified below after alkali saponification of the fats and oils. It is taken to include alcohols (other than glycerin), *e.g.*, sitosterol (phytosterol) in vegetable oils and cholesterol in animal oils and fats. Certain fish oils from the shark and dog families contain unsaponifiable hydrocarbons (squalene, spinacene, etc.). Some waxes yield insoluble alcohols on treatment with alkalis. The unsaponifiable matter generally remains dissolved in the soap solution after saponification. The principle of the method of estimation depends on the solubility of the unsaponifiable matter in ether or in petroleum ether, whereas the soaps are practically insoluble, whether they are in solution or in the dry state. It is better to use ether than petroleum ether, and to get rid of any soap, which may have been taken up into the ether by wax alcohols or hydrocarbons, by treatment with a little water and re-extraction with ether. For the experimental details reference may be made to the Report of the Committee of Analysts on the standard methods of analysis of seeds, nuts and kernels, fats and oils and fatty residues (Ministry of Food, Oils and Fats Branch);¹² also to Boemer's method.¹³ The amount of unsaponifiable matter in natural oils and fats is very variable, but in genuine samples it is quite small; *e.g.*, linseed oil, raw or refined, and soya oil (crude or edible) each contain about 1 per cent., and raw and refined linseed oils ought not to have more than $1\frac{1}{2}$ per cent.

Moisture.—The amount of moisture contained in a drying oil is variable, depending on its age and period of tanking. A good linseed oil should not contain more than 0.25 per cent. of moisture. The method of determination of the moisture is given in the Report of the Committee of Analysts mentioned above. A current of hydrogen is passed over asbestos saturated with the oil under

examination and the moisture is absorbed by concentrated sulphuric acid. In the opinion of the Committee this method is applicable to all fats and oils—to readily oxidisable oils like linseed oil, and to oils containing high percentages of free fatty acids of low molecular weight.

It is doubtful whether the whole of the moisture is removed by the above method when the oil contains much mucilage. In fats and oils which are free from uncombined fatty acids and are not readily oxidisable, the ordinary methods of drying on sand in a water oven may often be used.

Oxidised Fatty Acids.—Drying oils become viscous on exposure to air, owing to the formation of oxidised glycerides, and blown oils contain the same oxidation products. Their formation is accompanied by a reduction in the iodine value of the original oil. The estimation of the oxidised glycerides produced on the drying of paint or varnish is of importance. Fahrion¹⁴ estimates the amount of oxidised acids in the following manner:—4–5 gms. of the sample are saponified with alcoholic potash; the alcohol is evaporated off; the soap is dissolved in hot water, transferred to a separating funnel and decomposed with hydrochloric acid. After cooling, the liquid is shaken with petroleum ether (b. p. below 80°) and is allowed to stand until it has completely separated into two layers. The insoluble oxidised fatty acids will be found to adhere to the sides of the funnel or to form a sediment in the petroleum ether layer. The aqueous layer is drawn off, the petroleum ether removed, if necessary, through a filter, and the oxidised acids washed with more petroleum ether to remove adhering fatty acids. If the amount of oxidised fatty acids be large, it is advisable to dissolve them in alkali, decompose the resulting soap with hydrochloric acid and shake out again with petroleum ether to remove any soluble fatty acids. The oxidised acids are then dissolved in warm alcohol or ether, the solution is evaporated in a tared dish, and the residue weighed. Linseed oil blown for 10 hours at 120° will contain 7.1 per cent. of oxidised acids. Linseed oil blown with oxygen until its iodine value is 58.8 contains 42.82 per cent. of oxidised acids.

Refractive Indices of Drying Oils.—The ease with which the refractive index can be determined makes the refractometer of importance in the examination of drying oils and varnish thinners. The refractive index does not give a perfectly reliable means of detecting adulteration, but in conjunction with other tests it serves to indicate whether a sample is genuine or not. For the use of the refractometer in the analysis of oils and fats reference must be

made to a paper by J. N. Goldsmith.¹⁵ The refractive indices of oils decrease with rise in temperature, and the mean temperature correction per degree Centigrade is 0.00036. It is customary to determine the refractive indices of fluid drying oils at 20—25° or 40°. The refractive index of Indian linseed oil at 20° is 1.4710.¹⁶ The difference in the refractive indices of raw oil and boiled oil is comparatively small. Polymerisation of linseed oil is accompanied by a marked rise in the refractive index. Linseed oil thickened at 260—280° in CO₂ (s. g. 0.969) has a refractive index 1.4911. Oxidation of the oil is accompanied by an increase in the refractive index.* The refractive index of China wood oil (1.5172) is considerably higher than that of linseed oil, and this serves to detect adulteration as the value of the refractive index is lowered. The difference between the figures for China wood oil and soya oil at 40° being 0.0402; the addition of 10 per cent. or even of 5 per cent. soya oil can be detected. More importance is attached in England to the determination of the refractive index of China wood oil as a test of purity than to the test of coagulation by heat. Instead of measuring the refractive indices of oils, it is sometimes preferable to determine the refractive indices of the corresponding acids.

In the examination of varnish thinners the refractometer is of use in analysing a large number of binary solvent mixtures; thus the percentage of white spirit in a mixture of turpentine and white spirit can be determined with fair accuracy from the value of the refractive index, because the relationship is expressed by a linear graph. It must be pointed out that the method is invalid when benzene is a component of the white spirit.

Optical Dispersion.—For mixtures of fatty oils and fatty acids the refractive index will give better results, but the measurement of the optical dispersion provides useful confirmatory evidence. The dispersive power (ω) of a substance is expressed by the ratio of the coefficient of dispersion to the index of refraction of the mean rayless unity. If n_C , n_D and n_F represent the refractive indices of a substance for the C, D and F lines of the spectrum, then the dispersion of the substance is $n_F - n_C$ for the F, C lines, and its dispersive power (ω) = $\frac{n_F - n_C}{n_D - 1}$.

The dispersive power of China wood oil is 0.371, linseed oil 0.0218, cotton-seed oil 0.0195, castor oil 0.019, coco-nut oil 0.0167, menhaden oil 0.0207. The values are of much less analytical importance than the refractive indices. The drying and semi-drying

* The refractive index of linseed oil increases from 1.480 to 1.495 in 8 day (A. P. Laurie, private communication).

oils are differentiated from non-drying oils and fats, but the distinction is not very marked. Oxidation of an oil increases the dispersion, while heating (polymerisation) produces a marked decrease, and this may afford a means of distinguishing oxidised from polymerised oils. The dispersive power is closely connected with the molecular structure; e.g., benzene has a higher dispersive power than tetrahydrobenzol and hexylene; naphthalene than benzene and quinoline than naphthalene.

Hexabromide Test for Linseed and Other Oils.—When treated under proper conditions with bromine, the unsaturated oils or acids absorb 2 atoms of the halogen for each unsaturated linkage. The solubility of the bromo-derivatives in ether decreases with increased bromine content; so that the hexa- and octo-bromides are only very sparingly soluble, whereas the di- and tetra-bromo-derivatives are soluble. The fatty acids are generally used, because the glyceryl esters do not give concordant results. Many investigators have examined the conditions under which bromine is absorbed by unsaturated oils and acids. Hehner and Mitchell¹⁷ have investigated the combination with glycerides, Eibner¹⁸ and Muggenthaler¹⁹ the compounds formed with fatty acids. Eibner's method has been slightly modified by G. W. Thompson.²⁰ Bailey and Baldsiefen²¹ have examined the published methods for the hexabromide value, and find that the results obtained are not concordant. They recommend precautions in the preparation of the fatty acids and in the preparation of the hexabromide, and suggest the following method:—

(a) *Preparation of Fatty Acids.*—Approximately 50 gms. of oil are weighed into a 2-litre round-bottomed flask and 40 c.c. of caustic soda solution (s. g. 1.4) and 40 c.c. of alcohol added. The mixture is heated on a steam-bath for about half an hour, a stream of carbon dioxide being passed through the apparatus all the while. One litre of hot distilled water is added and the soap solution boiled, either over a free flame or on a steam-bath, to remove the alcohol. The solution is then cooled slightly and acidified with dilute hydrochloric acid (1:1). The mixture is warmed until the fatty acids form a clear layer, the current of carbon dioxide being continued. The fatty acids are separated from the aqueous layer in a separating funnel, and washed thoroughly with hot distilled water until the washings are neutral to methyl-orange. The warm fatty acids are freed from water by centrifuging and kept in a well-stoppered bottle.

(b) *Preparation of the Hexabromides.*—One gm. of fatty acids is accurately weighed into a tared centrifuge tube (1 inch diameter

and 5 inches long), and dissolved in 25 c.c. of specially prepared ether. [Methylated ether is washed with 10 per cent. of its volume of ice-cold distilled water. After separating the water and repeating the washing three times the washed ether is dried over fused calcium chloride and the drying completed by sodium. After distillation the ether is treated with an excess of finely-powdered hexabromide of the fatty acids of linseed oil previously prepared. The ether solution, kept at least for 3 hours at 0°, is decanted into a dry bottle.]

Bromine solution (5 c.c. of bromine in 25 c.c. of glacial acetic acid made up just before use) is added very slowly to the fatty acids dissolved in ether until a deep red colour is produced. The tube is then allowed to stand in an ice-chest over-night. The solution is separated from the precipitate by centrifuging, and the precipitate repeatedly washed with the specially prepared ether and the last traces of the ether removed in a vacuum. The precipitate is then weighed.

Steele and Washburn²² have slightly modified the method by the introduction of special precautions, and the results are considered by them to be more satisfactory than those obtained by Bailey.

The following table shows the percentages of insoluble bromides obtained from drying oils or their acids:—

	From glycerides. %.	From the acids. %.
Perilla oil	53	64 (Eibner)
Linseed oil:		
Iod. val. 181	23.1—23.5	42.0—50 (Steele and Bailey)
" " 204	49.3	
" " 190.4	37.72	
Tung oil	0	0
Menhaden oil	61.8	51.5 (Gemmell)
Soya-bean oil	3.7	4.2—6.5 (Steele and Bailey)

Mixtures of linseed and fish oil can be detected by the characteristic fishy odour produced on heating. Small quantities, not below 5 per cent., can be detected by Eisenschiml's test,²³ which depends on the production of an insoluble octobromo-compound by the action of bromine at 100°.

The Comparison of the Drying Time of an Oil against a Standard Linseed Oil.—The method employed consists in the determination of the time of drying and the condition of the dried surface of a

film of the oil which has been treated with siccatives. In a recent War Office Specification (C.W.D./404, 1920) for raw linseed oil, nine volumes of the oil are mixed with one volume of a 25 per cent. solution of precipitated manganese resinate in turpentine, and the mixture exposed in the form of a thin film on glass, in a vertical position at a temperature of 15.5° . The film must dry in a manner not inferior to that of a film of the approved tender sample, when tested at the same time and under identical conditions (see p. 99). Attention must be paid to the quality and appearance of the film, because some drying oils—*e.g.*, perilla—give peculiar surfaces with irregular markings. It will be found in the comparison between Baltic linseed oil and Indian linseed oil that the film of a drying oil of the former variety is harder and dries in a shorter time under the same conditions. The iodine value of Baltic oil is generally higher than that of Indian oil.

The film shall be considered to be surface dry when sand, which passes a 30-mesh I.M.M. sieve, but is retained by a 60-mesh I.M.M. sieve, when powdered on to the surface and allowed to remain thereon one minute can be easily removed by means of a camel-hair brush.

Mucilage.—The determination of the mucilage is of importance as indicating whether the oil is fresh or has been matured by tanking to allow the deposition of water and "foots." The amount present in a sample of oil can be determined in the following manner: 15 c.c. of the oil is placed in a test-tube ($\frac{5}{8}$ in. \times 6 inches) and heated over an open flame to 300° , the temperature being determined by a thermometer suspended in the oil. The rise in temperature should not exceed 50 degrees per minute. A linseed oil containing mucilage "breaks" at 260° and flakes of the mucilage appear. The oil is then cooled down to the ordinary temperature and at once centrifuged in graduated tubes. A good linseed oil shows 2—3 per cent. of mucilage by volume. If the oil be allowed to stand over-night after breaking, the "foots" cannot be removed by centrifuging. Other methods have been proposed by Walker and Weitz²⁴ and by C. D. Holley.²⁵

Colour.—The colour of linseed oil can be standardised by a Lovibond's tintometer. The American method of comparison of the colour of a drying oil with that of a solution of 1 gr. in 100 c.c. of pure sulphuric acid (s. g. 1.84) is, in the opinion of one of the authors, too low a standard for linseed oil which would be used in varnishes.²⁶ Reduction in the concentration of the potassium bichromate in sulphuric acid is accompanied by a slight greenish tinge which renders the comparison uncertain. One of the authors

suggests that a solution of iodine in pure potassium iodide (freshly prepared) will provide a more reliable comparison, especially for pale oils. Iodine in potassium iodide has been recommended as a more convenient standard for colour than potassium bichromate in sulphuric acid in the case of varnishes. The following concentrations of the iodine solutions are recommended for pale oils :—

0.0034 Gm. I with 0.051 gm. pure KI in 100 c.c. water equals in colour a clarified good linseed oil.

0.0114 Gm. I with 0.171 gm. pure KI in 100 c.c. water equals in colour a clarified poor oil.

0.0464 Gm. I with 0.696 gm. pure KI equals in colour an average raw linseed oil.

0.817 Gm. I with 0.0355 gm. pure KI equals in colour a refined artists' walnut oil.

As in the potassium bichromate method, the solution of iodine in potassium iodide must be freshly prepared. The test is carried out in glass tubes about 1 cm. diam. and 7—9 cm. in length.

Viscosity.—The viscosity of a drying oil may be determined by any of the methods used for the determination of the viscosity of varnishes (see p. 253).

Linseed Oil Substitutes.—The methods just described can also be employed in the examination of oils suspected of adulteration. When the price of linseed oil is high, adulterants appear. If the sample under examination has an abnormal drying time, specific gravity, iodine value and saponification value, adulterants may be suspected. The possible impurities are rosin oil, mineral oils—*e.g.*, light petroleum, kerosene or lubricating oil, fish oils, soya-bean oil, corn oil, and hemp or rape oil. The cheapest and commonest adulterants are the mineral oils, which have lower sp. gr. than linseed oil and reduce its saponification value as well. Rosin oil is frequently added to compensate for this reduction. The most objectionable linseed oil substitutes are those consisting of solutions of rosin and hydrocarbon oils with which are mixed tar-oil and rosin; such vehicles possess little permanence. Rosin would be indicated by the high acid value of the oil and by the Liebermann-Storch test. Corn oil is sometimes used as a substitute in Canada, but as it is a semi-drying oil, it will tend to delay the hardening of the film. The presence of soya oil will reduce the iodine value and the drying time. Other substitutes are obtained by dissolving metallic resins in tar-oil and petroleum. Raw soya oil as a substitute for linseed oil is preferably first blown, then given a heat treatment to thicken it, and a drier of manganese, cobalt linoleates in the proportions of 0.03, 0.02 and 0.01.

stearic and palmitic, are completely separated at -18° from a liquid acid such as lauric acid. Arachidic and lignoceric acids are separable at -18° from the acids of arachis oil. David (*loc. cit.*) maintains that the ammonium salts of the solid fatty acids and the ammonium salts of the liquid fatty acids are completely insoluble and soluble respectively in a large excess of ammonia at $13-14^{\circ}$. The acids are dissolved in warm 95 per cent. alcohol, and aqueous ammonia is added and the liquid heated until bubbles of ammonia vapour appear.

The clear solution is allowed to stand at 14° (not above) overnight and filtered. He claims that stearic, palmitic, hydroxystearic, lauric, arachidic and iso-oleic acids all form insoluble ammonium salts. According to Meigen and Neuberger, only about half the liquid acids are recovered in a pure state by any of the three methods just described. They recommend the precipitation of aqueous solutions of the potassium salts with excess of thallous sulphate, which brings down the solid saturated and solid unsaturated acids in a pure state. They claim that they can produce a 96 per cent. separation of oleic from stearic acid.³⁷

The separation of the components of the solid acids by the above method is yet unsatisfactory. A scheme of separation must include erucic, behenic, arachidic, stearic, palmitic and myristic acids. Erucic acid, $C_{22}H_{42}O_2$, m. p. $33-34^{\circ}$, gives a lead salt sparingly soluble in ether, and an iodine value of the solid acid obtained from the lead salt will furnish an approximate measure of its erucic acid content. Its reduction product, behenic acid, is characterised by its comparative insolubility in cold alcohol (100 parts alcohol dissolve 0.102 gm. at 17°). The detection and determination of rape oil in other oils are based upon the recognition of erucic acid. Tortelli and Forteni's test comprises the isolation of acids from lead salts insoluble in ether and determination of the iodine value. Holde and Marcusson's test³⁸ is based on the fact that erucic acid is more soluble in chilled alcohol (96 per cent.) than are other saturated solid acids.

Arachidic acid, $C_{20}H_{40}O_2$, may be detected and estimated in olive oils by Renard's process,³⁹ based on the sparing solubility of arachidic acid in 90 per cent. alcohol. The crude arachidic acid so obtained contains lignoceric acid, $C_{24}H_{48}O_2$, but no stearic acid. According to A. W. Thomas and C. I. Yu,⁴⁰ separation of stearic, arachidic and lignoceric acids may be effected by means of their magnesium salts, which are only slightly soluble in 90 per cent. (by vol.) alcohol, while the magnesium salts of oleic, linolic and

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respectively. Such an oil is considered to be a fair substitute for linseed oil.

Owing to the increasing demand for China wood oil, the detection of adulterants in the oil is of importance. The commonest are soya, perilla and lumbang (*Aleurites*) oils. The detection of the adulterants is based on: (1) differences in optical dispersion, (2) polymerisation or gelation tests. The high refractive index of China wood oil (1.5179 at 20°; linseed oil, 1.4835 at 15°) and the refractive indices of soya and perilla approaching the value of linseed oil make it easy to detect adulteration. The gelation test depends on the time taken for the oil under examination to set solid at a temperature of 293°. A sample of good tung oil should gelatinise in 10 minutes when tested according to Browne's directions.²⁷ The presence of free fatty acids will extend the time of gelation. It is possible to detect the presence of 5—10 per cent. of adulterating oil by means of the gelation test. The addition of lumbang oil will retard the solidification of the oil on heating and also reduce the refractive index. Perilla oil raises the iodine value, whereas soya oil depresses it, but both reduce the refractive index and retard the gelation of the oil.

The analyses of boiled and blown oils have been referred to in Chapter VI, and a comparison of the s. g., I.V. and insol. bromides are given in the table, which indicates also thickened (stand) oils:—

Oil.	S. G.	Iod. val.	Insoluble bromide. %.
Linseed oil	0.9308	186.4	24.17
Pale boiled oil	0.9429	171.0	20.97
Double boiled oil	0.9449	169.96	13.03
Linseed oil heated to 315°	0.9354	176.3	8.44
Linseed oil blown at 120° for 10 hrs.	0.9460	166.6	23.16
Ozonised oil (Baltic oil)	0.9310	180.1	36.26—36.34
Thin lithographic varnish	0.9691	125.3	2.00
Medium	0.9693	121.9	0.95

(Lewkowitsch, *Analyst*, 1904, 29, 334.)

The percentage of thickened linseed or thickened wood oil in a mixing may be determined by the acetone solubility method, which depends on the fact that 50 per cent. of the oil thickened under works conditions is insoluble in acetone.²⁸

The Examination of Mixtures of Drying Oils.—From the general characteristics of drying oils it will be seen that the glycerides

yield liquid non-volatile acids and a small amount of non-volatile solid acids containing saturated carbon atoms, with the exception of elæostearic and elaidic acids. Advantage is taken of the solubility of the unsaturated acids in certain solvents or the solubilities of their metallic salts of lead, potassium, cerium or thallium. The insolubility of the lead salts of the saturated acids in ether is the principle of Varrentrapp's method.²⁹ Lead α -elæostearate is insoluble in ether. The lead salts are also insoluble in petroleum ether, b. p. below 80°,³⁰ and in benzene.³¹ The details of the method are given by Lewkowitsch and Warburton.³² The principle of the method is to saponify the oil, precipitate the lead salts from the neutralised soap by lead acetate, and without drying them to extract with ether, and from the ethereal solution the unsaturated acids are obtained by means of dilute hydrochloric acid. From the insoluble lead salts the solid acids are obtained by boiling frequently with mineral acid to remove the last traces of metal. The separation is only approximate, as the accuracy of the results depends on the quantity of ether used and the temperature to which the ethereal solution of the lead salts is cooled. The following figures (Morrell) show the solubilities of the lead and cerium salts in ether :—

	Stearic acid.	Palmitic.	Oleic.	Elaidic.	Linolenic.	Linolic.	α -Elæostearic.	β -Elæostearic.
Lead salt	0.015%	0.018%	sol.	0.000%	sol.	sol.	73.4% insol.	—
Cerium salt ...	insol.	0.8% sol.	sol.	1.7% sol.	sol.	sol.	sol.	very slight sol.

W. Meigen and A. Neuberger³³ have tested the various published methods on known mixtures of solid and liquid fatty acids and conclude that none of them gives a reliable quantitative separation. They examined the methods of Bull and Fjellanger, of Fachini and Dorta and of David.³⁴ The method of Fachini and Dorta consists in the use of 90 per cent. acetone as a means of separating the potassium salts, since the salts of the solid acids are insoluble at the ordinary temperature, whereas the corresponding salts of the liquid acids are soluble. De Waele recommends using 10 gms. of the fatty acids dissolved in 90 c.c. of anhydrous acetone to which 10 c.c. of *N*-KHO are added and the insoluble salts are separated. Fachini and Dorta³⁵ also suggest the use of petroleum ether for the separation of the liquid and solid fatty acids, the liquid acids being soluble in all proportions in this solvent. The mixed fatty acids are dissolved in petroleum ether (1 part of acid in 100 parts of ether) and the mixture cooled for 1 hour at -40° , and the insoluble acids,

stearic and palmitic, are completely separated at -18° from a liquid acid such as lauric acid. Arachidic and lignoceric acids are separable at -18° from the acids of arachis oil. David (*loc. cit.*) maintains that the ammonium salts of the solid fatty acids and the ammonium salts of the liquid fatty acids are completely insoluble and soluble respectively in a large excess of ammonia at $13-14^{\circ}$. The acids are dissolved in warm 95 per cent. alcohol, and aqueous ammonia is added and the liquid heated until bubbles of ammonia vapour appear.

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linolenic acids are very soluble. The behaviour of the insoluble magnesium salts from rape and tung oils has also been studied.

The separation of stearic acid from palmitic acid may be effected by the method of Kreis and Hafner.⁴¹ For the identification and separation of the solid acids from linseed oil (stearic acid, 65 per cent., palmitic acid, 20 per cent.) reference may be made to J., 1913, 32, 1091). The separation of mixed saturated fatty acids occurring in drying oils is a very complicated problem, which in the examination of a drying oil is generally neglected, because of the small amount of the acids present. The technical methods depend on fractional crystallisation from alcohol, which is successful in the case of palmitic and stearic acids, but if myristic, behenic and arachidic acids be present the results are inconclusive. Better results may be expected by converting the fatty acids into their methyl esters and fractionally distilling them *in vacuo*, but the yield of solid saturated acids, which does not exceed 8—12 per cent. of the drying oil, renders the production of sufficient material for the fractionation of the methyl esters difficult. For further details the reader is referred to Lewkowitsch and Warburton (*loc. cit.*, p. 566). It is advisable to determine the iodine value of the saturated acids, because elæostearic forms a lead salt sparingly soluble in ether, and if that acid were present, the iodine value would be very appreciable.

The detection, separation and approximate determination of the liquid unsaturated fatty acids, oleic, linolic, linolenic, clupanodonic, which form lead salts soluble in ether, is described in detail in Eibner's communications on the analysis of linseed oil and fish oils (pp. 48 and 80). If oleic and linolic (elæostearic) acids be suspected, an iodine value of the mixed fatty acids will allow of estimation of the two acids as follows:—

$$x + y = 100; \frac{90.072}{100} + \frac{181.42y}{100} = \text{iodine value of mixed acids,}$$

x = percentage oleic acid; y = percentage linolic acid.

(I.V. linolic acid = 181.42.

I.V. oleic acid = 90.07.)

Hazura's method (*loc. cit.*) is uncertain, owing to the number of hydroxystearic acids obtainable and the variable yields. The bromine method as used by Eibner and Muggenthaler has yielded more satisfactory results. The method of fractionation of the methyl esters (p. 80) has been used in the examination of the acids in fish oil.

The hydroxylated fatty acids, of which ricinoleic acid, $C_{18}H_{33}O_2 \cdot OH$,

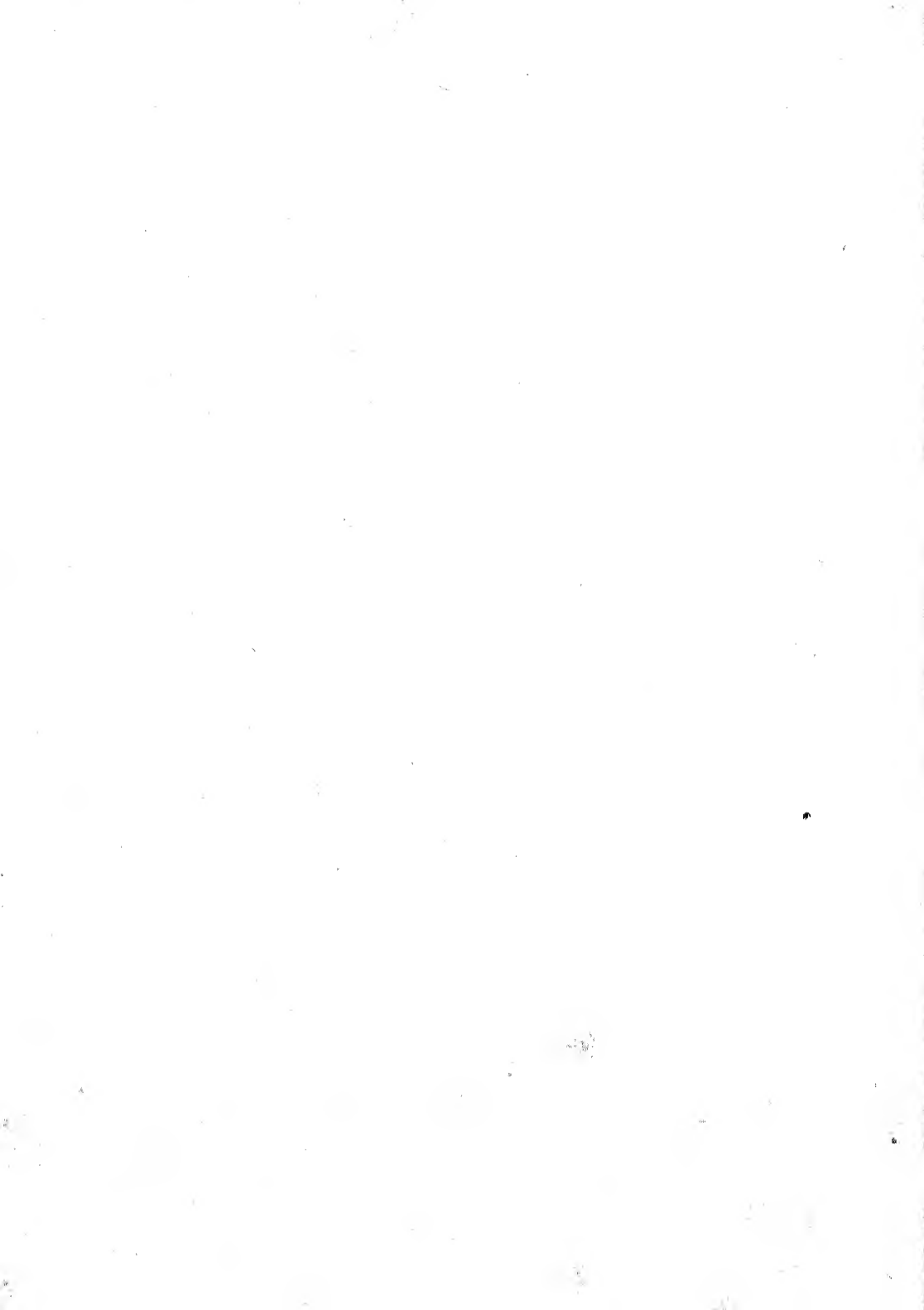
forms a lead salt insoluble in petroleum ether, will give an acetyl value on treatment with acetic anhydride.

	Acetyl Value.
Ricinoleic acid ($C_{18}H_{33}O_2 \cdot OH$)	165.0
Tetrahydroxystearic acid (sativic) ($C_{18}H_{32}O_2 \cdot (OH)_4$)	434.8
Hexahydroxystearic (linusic) ($C_{18}H_{30}O_2 \cdot (OH)_6$)	532.5

An important component of a drying oil is the variable oxidised fatty acids produced from exposure to the air. The method of Fahrion ⁴² is of importance, and the details of the method have been given on p. 205.

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